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(54) Title: PROCESS FOR PRODUCING POLYOLEFIN

(57) Abstract

A process for producing polyolefins having a controllable broadened molecular weight distribution utilizing transition metal metallocene catalyst systems, wherein the metallocene has at least one cyclopentadienyl ring which is substituted by a substituent having a 2° or 3° carbon atom through which it is covalently bonded to the cyclopentadienyl ring.

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TITLE: PROCESS FOR PRODUCING POLYOLEFIN

20   **FIELD OF THE INVENTION**

This invention relates to processes for olefin
polymerization and to the resultant polyolefin product,
particularly those having broadened molecular weight
distribution. Particularly, but not exclusively, this
25   invention also relates to the use of mixed
polymerization catalysts for controlling the molecular
weight distribution of a polymer.

BACKGROUND OF THE INVENTION

Olefin polymerization catalysts comprising a
30   metallocene and an aluminum alkyl component have long
been known. See, for example, AU-A-2436/88, DE-A-
2,608,863 published September 9, 1977, DE-A-2,608,933
published September 9, 1977, EP-A-0035242 published
September 9, 1991 and EP-A-129368 published September
35   9, 1991 which disclose catalyst systems which are
commercially useful for the polymerization of ethylene.
The molecular weight of the polymer product can be
controlled by adjusting the reaction temperature or the
amount of cocatalyst, or by the addition of hydrogen.

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The later publications require use of alumoxane or cocatalyst, which is produced by reacting an aluminum alkyl with water. Such reaction is very rapid and highly exothermic.

5   Alumoxanes may be prepared, for example, by adding extremely finely divided water, such as in the form of a humid solvent, to a solution of aluminum alkyl in benzene, other aromatics, or aliphatic hydrocarbons; or by reacting aluminum alkyl with a hydrated salt, such

10   as hydrated copper sulfate.

See U.S. Pat. Nos. 4,912,075, 4,937,301, 4,925,821, 4,937,217, 4,935,397 and 5,006,500 for teachings on alumoxane production.

U.S. Patent No. 5,006,500 describes procedures by

15   which an alumoxane is produced directly on a silica support by reacting an alkyl aluminum with water-containing silica. Such alumoxane-silica product is then reacted with a metallocene to yield a supported metallocene-alumoxane catalyst useful in the

20   polymerization of olefins.

Catalyst components comprising titanium and zirconium metallocenes produce polymers having a typically narrow molecular weight distribution (MWD), i.e. M_w/M_n. Although there are many commercial

25   applications for polyolefins with a narrow MWD as a desirable property, it is often desirable to have a polyolefin with a broader MWD, for example to ease the processability of polyolefins into finished form. The above cited publications neither disclose polyethylenes

30   having a broad MWD nor how to obtain such polyethylenes.

A method of broadening the molecular weight distribution of polyolefins has long been desired by and needed in the industry. For many applications, such

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as extrusion and molding processes, it is highly
desirable to use polyolefins which have a broad MWD.
Such polymers have lower melt viscosity and can have
higher melt strength. Lower melt viscosity allows a

5   film producer to operate at lower extruder pressures
and temperatures, and with lower energy requirements.
Higher melt strength allows a film producer to operate
at faster blown film rates. At the same time such
polymers exhibit reduced melt flow perturbations.

10   Another need in the industry is a method to
improve the balance between those film properties
which increase and those which decrease as product
crystallinity increases. For example, in ethylene-
alpha-olefin copolymers, product crystallinity is

15   controlled by the alpha-olefin content. As
crystallinity increases, film tensile strength
measured at low film elongation increases, but
film tear resistance and impact resistance both
decrease. Tensile strength at low elongation is an

20   important film property when the film is used to
make bags, especially those with handles. As
tensile strength at low elongation increases, the
load which can be supported without severe
elongation of the bag wall and bag handles

25   increases. As tear and dart impact resistance
increase, the resistance to puncture and the load
which can be supported after a puncture has
occurred both increase.

         In addition, a method of increasing the tensile

30   impact strength of polyolefins while maintaining
processability has long been desired by and needed in
industry. Such a polymer with a balance of strength
and processability could be utilized for manufacturing
molded and film products which are stronger than the

prior art materials while requiring the same processing energy or cycle time, or could be utilized for manufacturing molded and film products which are as strong as the prior art materials with less processing

5 energy or cycle time.

Several methods in the past have been directed toward making broader molecular weight distribution polyolefins. U.S. Patent No. 4,310,648 discloses a catalytic reaction product of a titanium compound, a

10 zirconium compound, an organomagnesium compound and a halide source. The reaction product, a heterogeneous catalyst, when employed in combination with aluminum alkyl, is useful for the production, at high activity, of broad molecular weight polyethylenes.

15 It is sometimes also desirable to have a polyethylene having a narrow molecular weight distribution and a high molecular weight. For example, U.S. Patent No. 4,361,685 discloses the use of organic soluble chromium and zirconium compounds employed in

20 combination with a supported catalyst system comprising an organometallic activating agent and a trivalent or tetravalent titanium compound. The polymers obtained have a high molecular weight and a narrow molecular weight distribution.

25 In "Molecular Weight Distribution And Stereoregularity Of Polypropylenes Obtained With Ti(OC4H9)4Al2(C2H3)3 Catalyst System"; _Polymer_, Pg. 469-471, 1981, Vol. 22, April, Doi, et al. disclose propylene polymerization with a catalyst, which at

30 about 41°C obtains a soluble catalyst and an insoluble catalyst fraction, one with a "homogeneous catalytic centre" and the other with a "heterogeneous catalytic centre". Polymerization at that temperature obtains polypropylene having a bimodal molecular weight

distribution. Also, U.S. Patent No. 4,931,417 describes the use of bis(methyl-t-butyl cyclopentadienyl) zirconium dichloride to obtain atactic polypropylene, but has no teachings regarding the production of processable crystalline polymers, or polyethylenes.

U.S. Patent No. 4,808,561 discloses a metallocene polymerization catalyst having cyclopentadienyl rings substituted with hydrocarbyl groups such as alkyl, aryl, alkylaryl, or arylalkyl groups. However, this patent does not teach a method of making broad molecular weight distribution polyolefins.

U.S. Patent No. 4,935,474 discloses a method of obtaining polyethylene having a broad molecular weight distribution utilizing a catalyst comprising (a) at least two different metallocenes each having different propagation and termination rate constants for ethylene polymerizations and (b) an alumoxane. However, this U.S. Patent does not disclose or suggest a method which employs a single metallocene capable of producing a broad MWD polymer.

In spite of the methods known in the past for polymerizing broader molecular weight distribution polyolefins, there still exists a need in the art for an improved catalyst system and methods for making high quality polyolefins which also provide control over the broadened molecular weight distribution.

In addition to the need for providing broader molecular weight distribution polyolefins, there also exists a need in the art for an improved catalyst and method of making high quality polyolefins having improved tensile strength at low elongation and improved tensile impact strength, while maintaining or improving processability.

SUMMARY OF THE INVENTION

This invention is directed toward the polymerization of olefins, optionally with a comonomer, in the presence of an improved metallocene catalyst

5   system which permits the molecular weight distribution of the polymer produced to be controlled to broadened form, to methods of making the improved catalyst system and to polymer products having broad MWD, improved tensile impact strength and other properties.

10 Accordingly, the present invention provides a process for producing polyolefins which comprises

(a)   contacting olefin monomer, optionally with co-monomer, with a catalyst system comprising:

(i)   a first transition metal metallocene

15 having a substituted cyclopentadienyl ring, the substituent of which is a hydrocarbon group or substituted hydrocarbon group comprising a 2° or 3° carbon atom through which it is bonded to the ring; and

(ii) an activator for the metallocene, under

20 polymerizing conditions, to form the desired polyolefin product.

The catalyst system may comprise more than one first transition metal metallocene. Optionally the catalyst system may also comprise one or more second

25 transition metal metallocenes having a substituted or unsubstituted cyclopentadienyl ring. When the second metallocene has a substituted cyclopentadienyl ring, the substituent may be of the same general description as the substituent of the first metallocene, or it may

30 be different. When it is of the same general description then the second metallocene is in effect simply an additional first metallocene. The catalyst systems of this present invention has an activator selected from ionic activators or alumoxane or

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combinations thereof. The key to the invention is that
the defined first metallocene structure includes a
substituent which leads to the production of polyolefin
product of broadened MWD, for example greater than 4.

5   The optional second metallocene enables further control
over the product MWD, since its molecular structure
will have a modifying or additive effect to the effect
of the defined first metallocene. Adjustment of the
molar ratio between the first and second metallocenes

10   permits tailoring of the MWD of the polymer.
Preferably the first metallocene and/or the optional
second metallocene is a bridged bis-cyclopentadienyl
metallocene, wherein at least one of the
cyclopentadienyl rings carries a substituent other than

15   the bridging moiety. The final molecular weight
distribution will be some value between the highest and
the lowest molecular weight distribution that each
substituent would produce if used alone.

By practicing the process of the invention, in a
20   preferred embodiment, ethylene is polymerized to
produce high molecular weight polyethylenes such as
linear low density polyethylene (LLDPE) and high
density polyethylene (HDPE) polymers having broadened
molecular weight distributions with improved

25   mechanical, physical and/or chemical properties. The
polymers produced by this present invention are useful
for fabrication into articles by, for example,
extrusion, injection molding, thermoforming, rotational
molding or film blow molding.

30   According to one embodiment of the present
invention, at least one monomer of an olefin is
polymerized, preferably in, but not limited to, a gas-
phase reactor, in the presence of a supported catalyst
system having at least one transition metal metallocene

selected from Group IVB, Group VB or VIB metals of the Periodic Table of Elements. The process of this invention is suitable for use in slurry or solution reactors with an unsupported or a supported catalyst

5 system as well as gas phase reactors. In the preferred embodiment of the present invention, the broadening of the molecular weight distribution and the increase in the tensile impact strength is accomplished where the hydrocarbon substituent on a cyclopentadienyl of the

10 first metallocene is an alkyl having 3 to 20 carbon atoms and having a 2° (secondary) or 3° (tertiary) carbon atom with which it is covalently bonded to the ring.

BRIEF DESCRIPTION OF THE DRAWINGS

15   The foregoing objects, features, embodiments, and advantages of the invention will become clearer and more fully understood when the following detailed description is read in conjunction with the accompanying drawings, in which:

20   FIG. 1 is a 1H NMR(400MHz) trace for (t-BuCp)ZrCl2 showing the methyl protons of the t-butyl at about 1.25 parts per million (ppm) and showing the protons of the Cp ring at about 6.3 ppm.

        FIG. 2 is a 1H NMR(400MHz) trace for (i-PrCp)ZrCl2

25 showing the methyl protons of the i-propyl at about 1.20 ppm, the methine proton of the i-propyl at about 3.1 ppm, and showing the protons of the Cp ring at about 6.2 ppm.

        FIG. 3 is a plot of log viscosity vs. log

30 molecular weight for polymers produced by the process of this invention (solid dot) and for conventional polymers produced by a heterogeneous catalyst of the conventional Ziegler-type catalyst.

FIG. 4 is a plot of tensile impact vs. log molecular weight for polymers produced by the process of this invention (circles) and for conventional polymers produced by a heterogeneous catalyst of the

5   conventional Ziegler-type catalyst (solid dots). The regression lines for the polymers produced by the process of this invention and for the conventional Ziegler-type catalyst type polymers are represented by dots and dashes, respectively.

10   FIG. 5 is a plot of tensile impact ratio vs. log molecular weight for the polymers produced by the process of this invention and for conventional Ziegler-type catalyst type polymers.

FIG. 6 is a graph of the solubility distribution

15   and composition distribution of a copolymer (X) having a narrow SDBI and CDBI and copolymer (Y) having a broad SDBI and CDBI.

FIG. 7 is a graph illustrating the correlation between dissolution temperature and composition used

20   to convert the temperature scale to a composition scale.

FIG. 8 is a graph illustrating the method for calculating CDBI.

FIG. 9 is a graph illustrating melt tensile force

25   versus molecular weight for the polymer produced by the process of this present invention.

FIG. 10 is a plot illustrating stress versus elongation for the polymer produced by the process of this present invention.

30   **DETAILED DESCRIPTION OF THE INVENTION**

The catalyst components can be activated by ionic activators or alumoxane or combinations thereof.

In a preferred embodiment of the invention two metallocenes are employed as component (i) of the

catalyst system, since this permits good control of polymer product MWD. If the second metallocene, preferably a bis cyclopentadienyl transition metal compound, has at least one cyclopentadienyl ring

5 substituted through a 2° or 3° carbon, then the system contains two "first" metallocenes; if the second metallocene does not have such a substituent then the system comprises a "first" and a "second" metallocene. Either form is referred to as a "mixed" catalyst

10 system. The transition metal of the metallocenes can be the same or different.

The mixed systems contemplated by this present invention may be obtained by physical mixing, chemical mixing or chemical synthesis.

15 "Physical mixing" refers to physically mixing or blending two or more different types of supported or unsupported catalysts, for example, catalysts having different transition metals and/or different cyclopentadienyl ring substituents. For a mixture

20 comprising supported catalysts, the supported first metallocene is prepared independently from the supported second metallocene, then the two components are "physically" mixed together.

"Chemical mixing" refers to providing a mixture of

25 two or more different types metallocene on a single support. In particular, "chemical mixing" requires the mixing of at least two transition metal metallocenes first before introducing the support. As a result, the metallocene compounds are supported on the same

30 support. This is different from the "physical mixing" where the metallocene components are each supported separately and independently on different supports (although the support materials may in fact be the same).

10

"Synthesis mixing" refers to the provision of
different cyclopentadienyl ring substituents on one
transition metal metallocene catalyst component. Thus,
"synthesis mixing" describes a metallocene component

5   having at least one cyclopentadienyl ring with at least
two different substituents bonded to the at least one
cyclopentadienyl ring or a metallocene component having
at least two cyclopentadienyl rings where each ring is
substituted by a different substituent. These forms of

10 components must be carefully synthesized prior to their
use and hence the name "synthesis mixing".

The transition metal metallocene components
utilized in the process of this present invention may
be any of the organometallic coordination compounds

15 obtained as a cyclopentadienyl derivative of the
Group IVB, Group VB and Group VIB transition metals.
Metallocenes which are useful for preparing an active
catalytic complex according to the process of this
invention are the mono-, bi- and tri- cyclopentadienyl

20 metal compounds and most preferably, bis-
cyclopentadienyl compounds. Also suitable are bridged
cyclopentadienyl compounds.

It is essential that the improved catalyst system
of the process of the present invention has a

25 metallocene component that comprises at least one first
transition metal metallocene wherein at least one
cyclopentadienyl ring in the system is substituted with
a first hydrocarbon substituent that functions as an
MWD broadening substituent. This hydrocarbon

30 substituent has a 2° or 3° carbon atom through which it
is covalently bonded to the cyclopentadienyl ring.
Preferably the catalyst system also has another
metallocene component, which has at least one
cyclopentadienyl ring substituted with a second

cyclopentadienyl ring substituent different from the
first ring substituent of the first metallocene
component. Preferred metallocenes are the bis
(cyclopentadienyl) Group IVB transition metal compounds
5   wherein at least one of the cyclopentadienyl groups of
the catalyst system of the present invention is
substituted with a hydrocarbon group by covalent
bonding through its 2° or 3° carbon atom.

   Examples of metallocenes particularly useful in
10   the process of this invention are those represented by
the general formulas:

     I. $(C_5R'k)gR''s(C_5R'k)MQ_{3-g}$, and

15   II. $R''(C_5R'4)_2MQ$
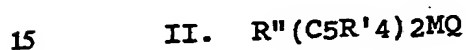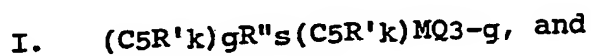
wherein $(C_5R'k)$ is a substituted or unsubstituted
cyclopentadienyl, M is a Group IVB or VB transition
metal and preferably a Group IVB transition metal, each
20   group R' is H, a hydrocarbon group or a substituted
hydrocarbon group with at least one substituent R' on
one cyclopentadienyl ring of the catalyst system being
a hydrocarbon or substituted hydrocarbon group
comprising a 2° or 3° carbon atom through which it is
25   bonded to the cyclopentadienyl group. Other
substituents R' in the catalyst system may be hydrogen,
one or more of the specified 2° or 3° carbon containing
groups, or a different groups, for example a
hydrocarbyl radical such as alkyl, alicyclic, aryl,
30   alkylaryl, or arylalkyl radicals containing from 1 to
20 carbon atoms, a silicon-containing hydrocarbyl
radical, or a hydrocarbon radical bonded to two carbon
atoms of the ring to form a fused ring system, for
example the cyclopentadienyl ring and a C4-C6 ring such

as indenyl, R" represents a bridging moiety (optional in formula I) between two cyclopentadienyl rings, for example C_1-C_4 alkylene radical, a dialkyl or silicon containing group such as dihydrocarbyl (for example dialkyl germanium or silicon, or a phosphine or amine radical bridging any one pair of the rings, Q may be a hydrocarbyl radical such as aryl, alkyl, alicyclic, alkenyl, alkylaryl, or arylalkyl having 1-20 carbon atoms, hydrocarboxyl radical having 1-20 carbon atoms or halogen and can be the same or different or two Q's may be an alkylidene radical having from 1 to about 20 carbon atoms. In formula (I) s is 0 or 1 depending on whether the bridge is present, g is 0, 1 or 2; when g is 0, s is 0; k is 4 when s is 1 and k is 5 when s is 0.

Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, cyclohexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, ethylhexyl, phenyl, and the like. Exemplary alkylene radicals are methylene, ethylene, propylene, and the like. Exemplary halogen atoms include chlorine, bromine and iodine and of these halogen atoms, chlorine is preferred. Exemplary alkylidene radicals are methylidene, ethylidene and propylidene.

Of the metallocenes, hafnocenes, zirconocenes and titanocenes are most preferred.

Examples of suitable preferred catalyst systems comprising bis(cyclopentadienyl) Group IVB transition metal compounds wherein at least one of the cyclopentadienyl rings of the system has a substituent hydrocarbon or substituted hydrocarbon group covalently bonded to the ring through a 2° or 3° carbon atom, are represented by the following general formulas:

III. (A-Cp)MX1X2

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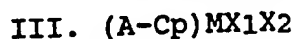
IV.   (A-CP)MX'1X'2

V.   (A-Cp)MJ

VI.   (Cp*)(CpR)MX1

wherein "Cp" represents a cyclopentadienyl radical

5   which may be substituted or unsubstituted, and:

(A-Cp) is either (Cp)(Cp*) or Cp-A'-Cp* and Cp and
Cp* are the same or different cyclopentadienyl
ring substituted with from one to five substituent
groups R, with at least one substituent R group in

10 the catalyst system being a molecular weight
distribution broadening or tensile impact strength
enhancing substituent comprising a 2° or 3° carbon
atom with which it is bonded to the
cyclopentadienyl group. Preferably the metallocene

15 has at least one second substituent R group which
is not hydrogen and is different from the first
substituent R group, with the second substituent R
group and each remainder group R being
independently, a radical which can be hydrocarbyl,

20 halocarbyl, substituted halocarbyl, hydrocarbyl-
substituted organometalloid, or halogen, or Cp and
Cp* are a cyclopentadienyl ring, with at least one
group R on the metallocene compound being a
molecular weight distribution broadening or
tensile impact strength enhancing substituent

25 comprising a 2° or 3° carbon atom with which it is
bonded to the cyclopentadienyl ring, with a second
substituent R group being different than the first
substituent R group, and in which two of the
remainder adjacent R groups are joined forming a

30 C4 to C20 ring to give a saturated or unsaturated
polycyclic cyclopentadienyl ligand such as
indenyl, tetrahydroindenyl, fluorenyl, or
octahydrofluorenyl and A' is a covalent bridging

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group which restricts rotation of the two Cp-
groups, M is titanium, zirconium or hafnium; J is
an olefin, diolefin or aryne ligand; X_1 and X_2
are, independently, selected from the group
consisting of hydride radicals, hydrocarbyl
radicals having from 1 to about 20 carbon atoms,
substituted-hydrocarbyl radicals having from 1 to
about 20 carbon atoms, wherein one or more of the
hydrogen atoms are replaced with a halogen atom,
organometalloid radicals comprising a Group IV-A
element wherein each of the hydrocarbyl
substitutions contained in the organic portion of
said organometalloid, independently, contain from
1 to about 20 carbon atoms and the like; X'_1 and
X'_2 are joined and bound to the metal atom to form
a metallacycle, in which the metal atom, X'_1, and
X'_2 form a hydrocarbocyclic ring containing from
about 3 to about 20 carbon atoms; and R is a
substituent, preferably a hydrocarbyl substituent,
on one of the cyclopentadienyl radicals which is
also bound to the metal atom.

Each carbon atom in the cyclopentadienyl radical ("Cp")
may be, independently, unsubstituted or substituted
with the same or a different radical selected from the
group consisting of hydrocarbyl radicals, substituted-
hydrocarbyl radicals wherein one or more hydrogen atoms
is replaced by a halogen atom, hydrocarbyl radicals in
which adjacent substituents are joined to form a ring
of 4 to 10 or more carbon atoms, hydrocarbyl-
substituted metalloid radicals wherein the metalloid is
selected from Group IV or V of the Periodic Table of
the Elements, and halogen radicals. Suitable
hydrocarbyl and substituted-hydrocarbyl radicals, which
may be substituted for at least one hydrogen atom in a

cyclopentadienyl radical, contain from 1 to about 20
carbon atoms and include straight and branched alkyl
radicals, cyclic hydrocarbon radicals, alkyl-
substituted cyclic hydrocarbon radicals, aryl
5 substituted radicals and alkyl aryl-substituted
radicals. Similarly, and when X_1 and/or X_2 is a hydro-
carbyl or substituted-hydrocarbyl radical, each may,
independently, contain from 1 to about 20 carbon atoms
and be a straight or branched alkyl radical, a cyclic
10 hydrocarbyl radical, an alkyl-substituted
cyclohydrocarbyl radical, an aryl radical or an alkyl-
substituted radical. Suitable organometalloid radicals
include mono-, di- and tri- substituted organometalloid
radicals of Group IV or V elements wherein each of the
15 hydrocarbyl groups contain from 1 to about 20 carbon
atoms. More particularly, suitable organometalloid
radicals include trimethylsilyl, triethylsilyl,
ethyldimethylsilyl, methyldiethylsilyl, triphenyl-
germyl, trimethylgermyl and the like.
20   Hydrocarbon substituents suitable as the molecular
weight distribution broadening substituent of the first
metallocene "defined substituent" are generally any
optionally substituted hydrocarbon having from 3 to 20
carbon atoms that comprises a 2° or 3° carbon atom
25 through which the group is covalently bonded to the
cyclopentadienyl ring. Suitable hydrocarbons include,
for example, alkyl, alkenyl, aryl, alicyclic alkylaryl,
or arylalkyl groups. The designation "2° or 3° carbon
atom" refers to the classification of the carbon atom
30 if the substituent were a carbonium ion not bonded to
the cyclopentadienyl carbon atom. Of course once the
substituent is covalently bonded to the
cyclopentadienyl group, the classification of the
carbon atom changes (increases in degree), however, the

designation "2° or 3°carbon atom" is still utilized and refers to the substituent in its carbonium ion state and not its covalently bonded state. Preferably, the defined substituent is an alkyl having from 3 to 20

5   carbon atoms, more preferably, 3 to 7 carbon atoms , and most preferably 3 to 5 carbon atoms. and comprising a 2° or 3° carbon atom with which it is covalently bonded to the cyclopentadienyl ring. Exemplary defined substituents include tertiary butyl, isopropyl, and 2°

10 pentyl substituents. The tertiary butyl group comprises a 3° carbon atom at the 2nd position, and the isopropyl group comprises a 2° carbon atom at the 2nd position, through which they are respectively bonded to the cyclopentadienyl ring of the metallocene component.

15 The term "2° pentyl substituent" is herein intended to mean a pentyl group covalently bonded, or able to be bonded at any of the three middle carbons of the n-pentyl group. Preferably, the carbon atom at the 3rd position is used to connect the n-pentyl group to the

20 cyclopentadienyl ring.

The presence of a first metallocene in which at least one cyclopentadienyl ring carries the defined substituent has been found to confer on the polymerization process the ability to produce polymer

25 e.g. polyethylene or ethylene copolymers which have broader MWD than polymers produced using a metallocene not having the defined substituent. This recognition is surprising, and permits control of polymer properties by selection of the defined substituent on

30 the first metallocene. Further control is enabled by selection of other cyclopentadienyl ring substituents on the first metallocene; by the presence or absence of a second metallocene; and if present by selection of the substituent types on the substituted ring(s) of

the second metallocene. Methods of substituting hydrocarbon substituents onto a cyclopentadienyl ring of a metallocene are well known, and any suitable method may be utilized. Such methods include that of

5 Wailes, et al., *"Organometallic Chemistry of Titanium, Zirconium and Hafnium"* (1974).

Generally, such methods involve a salt of the cyclopentadienyl compound, such as a lithium or sodium salt, that is reacted with a halogen substituted

10 substituent. The halogen is removed from the carbon atom of the substituent by lithium or sodium and this carbon atom then covalently bonds to the cyclopentadienyl ring. For the present invention, this means that the halogen is substituted on the 2° or 3°

15 carbon atom. In the reaction, the halogen forms a salt with the lithium or sodium, and the substituent is substituted onto the cyclopentadienyl ring connected by the 2° or 3° carbon atom. The substituted cyclopentadienyl is then recovered from the reaction

20 mixture.

The process according to the invention comprises an activator component (ii) for the first metallocene component (i). Any activator which makes the first metallocene active for olefin polymerization may be

25 used, for example a trialkyl aluminum. Preferably the activator is an alumoxane or one of the class of ionic activators which in combination with the metallocene form a non-coordinating anion system. The catalyst system may be homogeneous or supported.

30 While not wishing to be bound by theory, alumoxanes are oligomeric aluminum compounds represented by the general formula $-(R-Al-O)y$, which may be a cyclic compound and $R(R-Al-O-)yAlR_2$, which may be a linear compound. In the general formula, "R" is a

C1-C10 alkyl group such as, for example, methyl, ethyl, propyl, butyl, or pentyl and "y" is an integer from 2 to about 50 and represents the degree of oligo-merization in the alumoxane. Preferably, R is methyl,

5 and the degree of oligomerization; "y," is preferably 4 to 25 and most preferably 6-25. In the preparation of alumoxanes by reacting methyl aluminum and water, it is believed that a mixture of linear and cyclic compounds is obtained. Generally, an alumoxane having a higher

10 degree of oligomerization will, for a given metallocene, produce a catalyst complex of a higher activity than will an alumoxane having a lower degree of oligomerization. Hence, one procedure by which alumoxane is produced, by direct reaction of an alkyl

15 aluminum with an undehydrated silica gel, should ensure the conversion of a bulk quantity of the alkyl aluminum to an alumoxane that has a high degree of oligomerization. The combination of alkyl aluminum with water, or in some cases, hydroxyl groups, as

20 supplied by alcohol, hydrated materials or bases, results in a mixture, alumoxane, which will be effective in the practice of this invention.

Ionic activator compounds which may be used as activator for the catalyst system employed in the

25 process of the invention are described in EP-A-0277003 and EP-A-0277004 published on August 3, 1988. The compound comprises a cation and an anion, the cation being one which is reactable with a non-cyclopentadienyl ligand of the metallocene to yield as

30 the reaction product a neutral ligand derivative, and a cationic metallocene species to which the anion of the activator compound is essentially non-coordinating. The cationic metallocene as associated with the non-coordinating anion is the catalytically active species

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of the system. The activator compound may be, for example, a cation and an anionic carborane, or the ion-exchange activator compound is comprised of a cation and an anionic coordination complex. The cation of the

5 ion-exchange reagents can in general be any cationic species which is capable of reacting with a negatively charged ligand on the first transition metal metallocene. When the ligand on the transition metal precursor is an alkyl, then cations known to abstract

10 alkyls from early transition metal complexes can be used such as triphenylcarbonium, oxonium, silver (I), anitinium and ammonium. The system is best described as a metallocene cation and a bulky, noncoordinating anion which is a salt of Bronsted acids containing a

15 non-coordinating compatible anion. The compatible non-coordinating anion means an anion which functions as a charge balancing anion in a catalyst system and does not transfer an anionic substituent or fragment thereof to any cationic species thereby forming a neutral Group

20 IV, V and VIB or Lanthanide metal product. Compatible anions are anions which are not degraded to neutrality during catalyst preparation or use. A preferred ion-exchange activators are comprised of an acidic ammonium cation and an anionic coordination complex derived from

25 boron having the general formula $[LH]^+[BArAr'XX']$ wherein $[LH]^+$ is a protonated tertiary amine, L is a tertiary amine, Ar, Ar', X, X' are aromatic hydrocarbyl radicals, preferably halogenated e.g. fluorinated, and X and X' may be hydride, halide or hydrocarbyl radicals

30 e.g. aromatic hydrocarbyl radicals, preferably halogenated e.g. fluorinated. The chemical structure of the catalytically active species is dependent upon the nature of the cation employed in the activator compound and upon the stoichiometric proportions in

which the metallocene and activator compound are reacted.   In some instances, the metallocene cation generated by the reaction exists as a three coordinate species, $ACpZX_1+$ (where ACp represents two

5   cyclopentadienyl ligands which are bridged or unbridged, the same or different, Z is a Group IVB metal, and X_1 is selected from the group consisting of hydride, aryl, hydrocarbyl, halocarbyl, or organic derivatives of organometalloid radicals), although it

10   is possible that the four coordinate species $ACpZX_1(L)^+$ (where L is a neutral Lewis base such as tertiary amine or metallocene) can form via the labile coordination thereto of the neutral Lewis base by-product or via a dimeric coordination to a neutral as yet unreacted

15   metallocene.   In both forms the metallocene cation is stabilized by ionic association to the non-coordinating anion provided by the activator compound while the neutral coordination ligand, either the neutral Lewis base by-product or a neutral metallocene dimerizing

20   ligand are very labile to displacement by an olefin or other polymerizable monomer.

The catalyst systems as described above are very active for the production of polyolefins without the need to employ quantities of activator compounds much

25   in excess of a stoichiometric ratio to the metallocene of 1:1.

When an alumoxane is employed as activator for the inventive process, the metallocene-alumoxane catalyst system may be prepared, for example, by any of the

30   methods well known in the prior art, for example, as taught in U.S. Pat. No. 4,701,432, 4,808,561, 4,912,075, 4,925,821 and 5,008,228. Such methods include preparing the alumoxane component of the active catalyst complex separately then adding it to a

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catalyst support material which is then treated with a
metallocene to form an active catalyst complex. The
alumoxane may be prepared by contacting water in the
form of a moist solvent with a solution of aluminum
5 trialkyl in a suitable organic solvent such as benzene,
other aromatics, or aliphatic hydrocarbons.

Another method for preparing the metallocene-
alumoxane catalyst system involves contacting the
aluminum alkyl with the metallocene followed by the
10 addition of wet silica. In another method, an aluminum
alkyl is contacted with a hydrated salt, such as
hydrated copper sulfate.

When a supported metallocene-alumoxane catalyst
system is employed in the present invention, this is
15 preferably prepared by direct reaction of an aluminum
trialkyl with the material utilized as the catalyst ·
support, e.g. a "wet" silica gel, which may be
undehydrated silica gel and/or water impregnated silica
gel.

20 Undehydrated or water impregnated silica gel
especially useful as the catalyst support is that which
has a minimum surface area of 10, 100 or 200 m2/g and a
maximum surface area of 400, 500 or 700 m2/g. The
silica preferably has a pore volume of 3 to 0.5 cc/g,
25 more preferably 2-1 cc/g, and an adsorbed water content
of from 0.5 to 10 weight percent. The particle size of
the silica is preferably from 10μm to 100μm, and more
preferably from 30μm to 60μm.

The water impregnated gel preferably has an
30 adsorbed water content of from 10 to 50 weight percent,
with the upper range more preferably 35 or 40, and a
lower range more preferably 20 or 35. The particle size
of the silica is preferably in the upper range of from
10μm or 30μm to 60μm or 100μm.

Water-impregnated silica gel may be formed by adding sufficient water to commercially available silica gel (Davison 948) to create an aqueous slurry. Because silica gel possesses many fine pores, it is

5 extremely adsorbent and will rapidly become saturated. Once the aqueous slurry is formed, excess water can be removed by filtration, followed by air drying, or only air drying, to a free flowing powder state. Drying at elevated temperatures is not recommended because it

10 could substantially decrease the amount of adsorbed water.

In one method of forming the supported catalyst, undehydrated or water impregnated silica gel is slowly added over time, to a stirred solution of aluminum

15 trialkyl, preferably trimethyl aluminum or triethyl aluminum, in an amount sufficient to provide a mole ratio of aluminum trialkyl to water of from 3:1 or 2:1 to 1:2 or 0.9:1. Also suitable for use as the aluminum trialkyl are tripropyl aluminum, tri-n-butyl aluminum,

20 tri-isobutyl aluminum, tri(2-methylpentyl) aluminum, trihexyl aluminum, tri-n-octyl aluminum, and tri-n-decyl aluminum. The solvents are preferably inert hydrocarbons, in particular a hydrocarbon that is inert with respect to the catalyst system. Such solvents are

25 well known and include, for example, isobutane, butane, pentane, hexane, isohexane, heptane, octane, cyclohexane, methylcyclohexane, toluene and xylene.

Upon addition of the wet silica gel to the solution of aluminum trialkyl, the water content of the

30 silica gel controllably reacts with the aluminum trialkyl to produce an alumoxane which is deposited onto the surface of the silica gel particles. The reaction of the aluminum trialkyl with the water content of the silica gel proceeds relatively quickly

but not explosively. The reaction may be safely conducted in conventional mixing equipment under a mantle of inert gas.

5   Once the alumoxane-silica component has been formed, a metallocene may be added to the slurried suspension of alumoxane-silica gel product to form the metallocene-alumoxane catalyst, or the alumoxane silica component may be additionally processed to further enhance the ultimate catalytic activity of the formed

10   catalyst.

Further processing would comprise drying the slurried suspension to remove the excess liquid, preferably drying the alumoxane-silica component to a powder, followed by reslurrying the alumoxane-silica

15   component with a hydrocarbon solvent that is inert with respect to the alumoxane-silica component, such as for example isobutane, butane, isopentane, pentane, isohexane, hexane, heptane, octane, cyclohexane, methylcyclohexane, toluene and xylene.

20   Once the suspension of alumoxane-silica gel is formed, either initially, or after reslurrying with the additional processing, a metallocene is added to the suspension of alumoxane silica gel product in an amount sufficient to provide a mole ratio of aluminum to

25   transition metal which is preferably from 1000:1 to 1:1, preferably from 300:1 to 10:1 and especially from 150:1 to 30:1. The mixture is stirred for about 30 minutes to about one hour at ambient or an elevated temperature of about 75°C to permit the metallocene to

30   undergo complete complexing reaction with the adsorbed alumoxane. Thereafter, the solvent is removed and the residual solids are dried, preferably at a temperature of 75°C or greater, to a free flowing powder. The free flowing powder comprises a silica gel supported

metallocene alumoxane catalyst complex of sufficiently high catalytic activity for use in the gas phase polymerization of olefins by conventional gas phase polymerization procedures.

5   By appropriate selection of the type and relative amounts of the metallocene and the aluminum trialkyl cocatalyst precursor, one can attain by the present method the particular active catalyst complex desired for any particular application. For example, higher

10   concentrations of alumoxane in the catalyst system generally result in higher molecular weight polymer product. For most applications the ratio of aluminum in the aluminum alkyl to total metal in the transition metal metallocene can be in the range of from 1500:1,

15   1000:1 or 250:1, to 1:1500 to 1:1, or 5:1.

      Following the addition of the metallocene to the alumoxane adsorbed on the silica gel solids, the solvent is removed by filtering or evaporation, and the residual solids are dried to a free flowing powder.

20   Drying of the residual solids may be conducted at a temperature up to about 85°C, and preferably at a temperature of about 75°C. The dried free flowing powder comprises a metallocene alumoxane complex adsorbed upon the surface of the silica gel support

25   particles. The dried state composition exhibits a level of catalytic activity useful for gas phase polymerization of olefins.

      The monomers that may be polymerized in the process of the present invention are selected from

30   among cyclic or acyclic olefins and cyclic or acyclic polyenes. Suitable alpha-olefins include those such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene and 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicesene,

and 4-methyl-1-pentene. These may be polymerized either alone or in combination. Preferably, ethylene is polymerized either alone or with at least one alpha-olefin having 3 or more carbon atoms.

In addition, the present invention may be utilized for the copolymerization of a mono-olefin with a polyene, e.g. a polyene having from 3 to 20 carbon atoms. Preferably, the polyene has from 4 to 20 carbon atoms, more preferably from 4 to 15 carbon atoms. Preferably, the polyene is a diene with a double bond in the alpha position and generally has from 3 to 20 carbon atoms, such as, a straight chain, branched chain or cyclic hydrocarbon diene preferably having from 4 to 20 carbon atoms, and more preferably from 4 to 15 carbon atoms, and most preferably from 6 to 15 carbon atoms. Most preferably, the diene is a non conjugated diene. Examples of suitable dienes are straight chain acyclic dienes such as: 1,3-butadiene, 1,4-pentadiene, 1,4-hexadiene, 1,6-octadiene, 1,7-octadiene, 1,8-nonadiene and 1,9-decadiene; branched chain acyclic dienes such as: 5-methyl-1,4-hexadiene, 3,7-dimethyl-1,6-octadiene, 3,7-dimethyl-1,7-octadiene and mixed isomers of dihydromyricene and dihydroocinene; single ring alicyclic dienes such as: 1,3-cyclopentadiene, 1,4-cylcohexadiene, 1,5-cyclooctadiene and 1,5-cyclododecadiene; and multi-ring alicyclic fused and bridged ring dienes such as: tetrahydroindene, methyl tetrahydroindene, dicyclopentadiene, bicycle-(2,2,1)-heaped-2-5-diene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as 5-methylene-2-norbornene (MNB), 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, 5-vinyl-2-norbornene and norbornene. Of the dienes typically

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used to prepare EPR's, the particularly preferred dienes are 1,4-hexadiene, 5-ethylidene-2-norbornene, 5-vinylidene-2-norbornene, 5-methylene-2-norbornene and dicyclopentadiene. The especially preferred dienes are

5   5-ethylidene-2-norbornene and 1,4-hexadiene.

The polymer of the present invention will have a density in the range of from about 0.88 to about 0.965 g/cm3, preferably in the range of from about 0.89 to about 0.93 g/cm3.

10   In the process of the present invention, the polymerization may be conducted by a solution, slurry, or gas-phase technique. Preferred temperatures are from 0°C to 200°C, or even higher; atmospheric, subatmospheric, or superatmospheric pressure conditions

15   may be used; and conventional polymerization adjuvants, such as hydrogen may be employed if desired. Preferably, the process of the present invention utilizes gas phase polymerization. It is generally preferred to use the catalyst system at a concentration

20   such as to provide at least 0.000001 percent, more preferably at least 0.00001 percent by weight of transition metal based on the weight of the monomer(s), in the polymerization of ethylene, alone or with one or more higher olefins. The upper limit of the percent by

25   weight of transition metal present is determined by catalytic activity and process economics.

A slurry or solution polymerization process can utilize sub- or superatmospheric pressures and preferably employs temperatures of from 40°C to 110°C.

30   In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene, alpha-olefin comonomer, hydrogen and catalyst are added. The liquid employed as the polymerization medium can be an alkane

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or a cycloalkane, such as butane, pentane, hexane, or cylclohexane, or an aromatic hydrocarbon, such as toluene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of the

5 polymerization and relatively inert. Preferably, hexane or toluene is employed. In one embodiment, ethylene, alpha-olefin comonomer, hydrogen and catalyst are added to the liquid medium and conditions adjusted to polymerize the monomers.

10 A preferred gas phase polymerization process of the invention utilizes superatmospheric pressure and temperatures in the range of from 50°C to 120°C. Gas phase polymerization can be performed in a stirred or fluidized bed of catalyst and product particles in a

15 pressure vessel adapted to permit the separation of product particles from unreacted gases. To produce polyethylene, thermostated ethylene, optional comonomer, optional hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated so

20 as to maintain the particles at a temperature of about 50°C to about 120°C. Triethylaluminum may be added as needed as a scavenger of water, oxygen, and other adventitious impurities. Polymer product can be withdrawn continuously or semi-continuously at a rate

25 such as to maintain a constant product inventory in the reactor. After polymerization and deactivation of the catalyst, the product polymer can be recovered by any suitable means. In commercial practice, the polymer product can be recovered directly from the gas phase

30 reactor. Residual monomer can be removed with a nitrogen purge, and used without further deactivation or catalyst removal.

Molecular weight distribution (MWD), polydispersity, or (Mw/Mn) are generally synonymous and

are useful indicators of processability as well as
indicators of molecular structure. Generally as MWD
increases, the processability of the polymer increases.
Also, generally as MWD increases some of the polymer
5 characteristics will degrade, conversely as MWD
decreases, generally, some polymer properties e.g.
strength, will improve, while the processability will
decrease.

These general trends may be altered in some cases
10 such as, for example, the instances in which the MWD is
multi-modal as described in U.S. Pat. No 4,530,914 to
Ewen, et al. Since MWD is essentially an average over
a range, a polymer displaying a multi-modal
distribution may offer a high molecular weight, good
15 processability, and yet still retain good strength in
the resulting polymer. For these reasons, it is likely
that polymers having upper limits in the higher ranges
of MWD, such as, for example, above 3, preferably in
the range of above 3 to 100 and higher, when obtained
20 by the practice of this invention, may have useful
properties as well as being easy to process.

In accordance with the process of the present
invention, polymer is obtained with a broadened
molecular weight distribution as compared to polymer
25 obtained utilizing known catalysts at same or similar
polymerization conditions. Generally the polymer will
have a molecular weight distribution greater than 4,
preferably greater than 5, more preferably greater than
6, and most preferably greater than 7.

30 Also, in accordance with the process of the
present invention the polymer product preferably has a
high molecular weight, weight to number average (Mw) of
greater than 50,000, preferably in the range of 60,000

to 200,000 and even more preferably between 80,000 to 180,000.

The polymer obtained in the present process can be extruded into water and cut into pellets or other

5 suitable comminuted shapes. Pigments, antioxidants, fillers, stabilizers, processing aids, and other additives, as are known in the art, may be added to the polymer.

According to the process of the present

10 invention, the molecular weight distribution of the polymer produced may be controlled by selecting the types of substituents on the cyclopentadienyl rings of the catalyst system. The molecular weight distribution of the polymer

15 formed by the present invention using an embodiment of the catalyst system which has two or more substituents on the cyclopentadienyl rings of the system will depend upon the molecular weight distribution that such substituents would produce

20 if utilized alone. When catalysts with different substituents are used to produce polymers, the molecular weight distribution of those polymers will be a function of the molecular weight distributions produced with each substituent by

25 itself. By varying the ratio of the weight-average molecular weights of the two fractions the MWD of the bi-substituent product can range from less than 4 to greater than 11.

Control can be established by varying the ratio of

30 the first hydrocarbon substituent to the second hydrocarbon substituent in the catalyst system. With multiple hydrocarbon substituents on the cyclopentadienyl rings of the catalyst system, the resulting polymer will have a molecular weight

distribution somewhere between the highest and lowest
molecular weight distribution value for the
substituents were they used alone.

Also in accordance with the process of the present
invention, polymer is obtained having improved impact
strength as compared to polymer obtained utilizing
prior art catalysts at the same or similar
polymerization conditions. For melt indexes less than
about 5 dg/min, densities less than about 0.93 g/cm3
and with about the same comonomer and comonomer
content, polymers produced by the present invention
generally have at least 200% the tensile impact
strength of polymers produced utilizing conventional
Ziegler-type catalysts. Preferably, the tensile impact
strength is at least 250%, most preferably at least
300% greater. As the melt index (MI) increases, this
improved impact strength phenomenon tends to be
diminished, and in fact will converge at high melt
indexes and densities. The polymers produced by the
process of the present invention will generally have a
MI of at least 0.5 ranging up to that MI at which the
impact strength is diminished. Typically the range may
be from 0.5 to 10. For film applications the MI is
preferably in the range of from 0.5 to 3.5, and for
molding applications the MI is preferably in the range
of from 5 up to that MI at which the impact strength is
diminished.

The polymers obtained in the present process
have significantly higher melt strength than products
produced with conventional Ziegler-Natta catalysts or
with metallocene catalysts which produce narrow MWD
products as can be seen from Table VII. Further, the
polymer product produced by this present invention has
a high film tensile force at low elongation as is

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illustrated in Figure 9. Also, the polymer obtained in
the present process can be extruded into water and cut
into pellets or other suitable comminuted shapes.
Pigments, antioxidants, fillers, stabilizers,
5   processing aids, and other additives, as are known in
the art, may be added to the polymer.

     The polymers produced by the process of the
present invention are capable of being fabricated into
a wide variety of articles, as is known for
10 homopolymers of ethylene and copolymers of ethylene and
higher alpha-olefins, including films and molded
articles and the like.

     The compositional distribution breadth index
(CDBI) for the polymers produced by the process of the
15 present invention is generally from 30 to 95 percent.
For polymers produced utilizing a high pressure process
the CDBI is generally from 70 to 95 percent,
preferably 75 to 95 percent, and most preferably from
80 to 95 percent. For polymers produced utilizing a
20 gas phase process the CDBI is generally from 50 to 75
percent, preferably from 55 to 75 percent, and most
preferably from 65 to 75 percent.

     The CDBI and homopolymer content are both
determined by the Temperature Rising Elution
25 Fractionation (TREF) technique described in U.S. Patent
No. 5,008,204 and Wild, et al., J. Poly. Sci. Ed., Vol.
20, p. 441, (1982). The solvent was
tetrachloroethylene, the temperature range was 0°C to
120°C. The CDBI is defined as the weight percent of
30 polymer molecules having a comonomer content within the
median molar comonomer content ±25%. High CDBIs
correspond to narrow short chain branching (SCB)
distributions. The homopolymer content, i.e. portion
containing no SCBs, is the weight percent eluting above

85°C column temperature, the temperature above which no SCBs are detected.

Solubility Distribution is measured using a column of length 164 cm and 1.8 cm ID (inner diameter) which

5 is packed with non-porous glass beads (20-30 mesh) and immersed in a temperature programmable oil bath. The bath is stirred very vigorously to minimize temperature gradients within the bath, and the bath temperature is measured using a platinum resistance

10 thermometer. About 1.6 g of polymer is placed in a sample preparation chamber and repeatedly evacuated and filled with nitrogen to remove oxygen from the system. A metered volume of tetrachlorethylene solvent is then pumped into the sample preparation chamber,

15 where it is stirred and heated under 3 atmospheres pressure at 140°C to obtain a polymer solution of about 1 percent concentration. A metered volume of this solution, 100 cc is then pumped into the packed column thermostated at a high temperature, 120°C.

20 The polymer solution in the column is subsequently crystallized by cooling the column to 0°C at a cooling rate of ⁻20°C/min. The column temperature is then maintained at this temperature for 25 min. at 0°C. The elution stage is then begun by pumping pure solvent,

25 preheated to the temperature of the oil bath, through the column at a flow rate of 27 cc/min. Effluent from the column passes through a heated line to an IR detector which is used to measure the absorbance of the effluent stream. The absorbance of the polymer

30 carbon-hydrogen stretching bands at about 2960 cm-1 serves as a continuous measure of the relative weight percent concentration of polymer in the effluent. After passing through the infrared detector the temperature of the effluent is reduced to about 110°C,

and the pressure is reduced to atmospheric pressure before passing the effluent stream into an automatic fraction collector. Fractions are collected in 3°C intervals. In the elution stage pure

5 tetrachlorethylene solvent is pumped through the column at 0°C at 27 cc/min. for 25 min. This flushes polymer that has not crystallized during the cooling stage out of the column so that the percent of uncrystallized polymer (i.e. the percent of polymer

10 soluble at 0°C) can be determined from the infrared trace. The temperature is then programmed upward at a rate of 1.0°C/min. to 120°C. A solubility distribution curve, i.e. a plot of weight fraction of polymer solubilized as a function of temperature, is thus

15 obtained.

The procedure for calculating the Solubility Distribution Breadth Index (SDBI) is set forth below.

Solubility distributions of two ethylene interpolymers are shown in FIG. 6. Here, for

20 illustration purposes only, Sample X has a narrow solubility distribution and elutes over a narrow temperature range compared to Sample Y, which has a broad solubility distribution. A solubility distribution breadth index (SDBI) is used as a measure

25 of the breadth of the solubility distribution curve. Let $w(T)$ be the weight fraction of polymer eluting (dissolving) at temperature T. The average dissolution temperature, T ave, is given by

30
$$Tave = \int T\, w(T)\, dT, \text{ where } \int w(T)\, dT = 1.$$

SDBI is calculated using the relation:

$$SDBI(°C) = [(T - Tave)^4 w(T)\, dT]^{1/4}$$

34

(SDBI is thus analogous to the standard deviation of the solubility distribution curve, but it involves the fourth power rather than the second power to T -

5   Tave). Thus, for example, the narrow solubility distribution Sample X and the broad solubility distribution Sample Y in FIG. 6 have SDBI values equal to 14.6°C and 29.4°C, respectively. The preferred values of SDBI are less than 28°C and more preferred

10   less than 25°C and even more preferred less than 20°C.

The composition distribution (CD) of a crystalline interpolymer is determined as follows. The composition and number average molecular weight, Mn, of fractions collected in various narrow temperature

15   intervals for several poly(ethylene-co-butene)'s was determined by C13 NMR and size exclusion chromatography, respectively. FIG. 7 is a plot of mole percent comonomer vs. elution temperature for fractions having Mn > 15,000. The curve drawn through

20   the data points is used to correlate composition with elution temperature for temperatures greater than 0°C. The correlation between elution temperature and composition becomes less accurate as the Mn of a fraction decreases below 15,000. Such errors can be

25   eliminated by direct measurement of the composition of effluent fractions by C13 NMR. Alternatively, the elution temperature-composition calibration for high molecular weight fractions given in Figure 7 may be corrected based on the Mn of effluent fractions and an

30   experimentally established correlation between Mn and elution temperature that applies for Mn < 15,000. However, it is assumed that such low molecular weight molecules are present to a negligible extent and that any errors caused are negligible. A correlation curve

35

such as the one in FIG. 7 is applicable to any
essentially random poly(ethylene-co-α-olefin)
provided, however, that the α-olefin is not propylene.

5   The temperature scale of a solubility distribution
plot can thus be transformed to a composition scale,
yielding a weight fraction of polymer versus
composition curve. As seen from the composition scale
in FIG. 7, Sample X contains molecules spanning a
narrow composition range, whereas Sample Y contains

10   molecules spanning a wide composition range. Thus,
Sample X has a narrow composition distribution whereas
Sample Y has a broad composition distribution.

A quantitative measure of the breadth of the
composition distribution is provided by the

15   Composition Distribution Breadth Index (CDBI). CDBI is
defined to be the percent of polymer whose composition
is within 50% of the median comonomer composition. It
is calculated from the composition distribution cure
and the normalized cumulative integral of the

20   composition distribution curve, as illustrated in FIG.
8. The median composition, C_{med}, corresponds to the
composition at the point where the cumulative integral
equals 0.5. The difference between the values of the
cumulative integral at compositions 0.5 C_{med} and 1.5

25   C_{med} (71 - 29, or 42%, in this example) is the CDBI of
the copolymer. CDBI values fall between zero and one,
with large values indicating narrow CD and low values
indicating broad CD. Thus, now referring back to
Figure 6, the narrow and broad CD copolymers have

30   CDBI's equal to 95.5% and 42%, respectively. It is
difficult to measure the CD and CDBI of copolymers
having very low comonomer content with high accuracy
so the CDBI of polyethylenes with densities greater
than 0.94 g/cc is defined to be equal to 100%.

Unless otherwise indicated, terms such as
"comonomer content", "average comonomer content" and
the like refer to the bulk comonomer content of the
indicated interpolymer blend, blend component or
5   fraction on a molar basis.

Hexane extractables is determined with a Soxtec
extractor on samples milled to 20-mesh. Each sample is
weighed, extracted with hexane at reflux conditions for
one hour, rinsed for two hours, dried and reweighed.
10   Weight percent hexane extractables is calculated from
weight loss. Hexane extractables captures not only low
molecular weight content, but also material with high
SCB frequencies, regardless of molecular weight.

Molecular weight profiles were determined using
15   Size Exclusion Chromatography. The included data was
obtained at 145°C with a Waters SEC using Ultrastyrogel
columns and a refractive index detector. The solvent
was trichlorobenzene; the calibration standards were
polystyrene. The key statistics are number-average
20   molecular weight (Mn), weight-average molecular weight
(Mw), Z-average molecular weight (Mz), polydispersity
index (Mw/Mn), and the Mz/Mw ratio.

Viscosity was measured with an Instron Capillary
Rheometer at 190°C at ten different shear rates ranging
25   from 13.7 s-1 to 13.7K s-1. Viscosity was measured to
reflect processability parameters such as extruder
power draw and head pressure. The first point of
discontinuity as shear rate increases in the shear
stress vs. shear rate curve is assumed to be the onset
30   of surface melt fracture, another key processability
parameter for linear polyethylenes.

Tensile impact was measured according to ASTM D-
1822.

Example 1 - PREPARATION OF METALLOCENE

Bis(η^5-n-propylcyclopentadienyl)zirconium (IV) dichloride {(n-PrCp)2ZrCl2}; bis(η^5-i-propycyclopentadienyl)zirconium (IV) dichloride {(i-PrCp)2ZrCl2}; bis(η^5-i-butylcyclopentadienyl(zirconium

5 (IV) dichloride {(i-BuCp)2ZrCl2}; bis(η^5-3-pentylcyclopentadienyl)(zirconium (IV) dichloride {3-PentCp)2ZrCl2} and bis(η^5-t-butylcyclopentadienyl) zirconium (IV) dichloride {t-BuCp)2ZrCl2} were prepared using similar procedures. For example, (t-BuCp)2ZrCl2

10 was prepared according to the following methods:

A 2-Bromo-2-methyl propane sample(353.5 g, 2.582 mol, Aldrich) was transferred into a 2-l reaction flask with side-arms at 5°C. Sodium cyclopentadienide (1290 cm3 of a 2.0 M solution in THF, 2.582 mol, Aldrich) was

15 slowly added. After complete addition, the reaction set-up was allowed to warm up to ambient temperature over 12 hours. Distilled water was added to dissolve the resulting sodium bromide and the THF solution was collected over anhydrous sodium sulfate. The aqueous

20 layer was repeatedly extracted with diethyl ether and combined with the THF solution. Filtration afforded the crude 2-cyclopentadienyl-2-methyl propane (t-BuCp); the solvent was removed and the crude product was fractionally distilled to obtain the pure (t-BuCp),

25 boiling point 125°C. A sample of the pure t-BuCp (42.81 g, 0.351 mol) and THF (400 cm3) were transferred into a 1-l reaction flask equipped with a mechanical stirrer. n-Butyl lithium (223 cm3 of a 1.6 M solution in hexanes, 0.357 mol, Aldrich) was added dropwise at

30 ambient temperature. The mixture was vigorously stirred for 3 hours and the resulting solution of t-BuC5H4-Li+ was slowly added to a suspension of ZrCl4 (40.78 g, 0.175 mol) in THF (100 cm3) at -78°C. After complete addition of the lithiated salt, stirring

continued and the reaction slowly warmed up to ambient temperature over 12 h. The solvent was stripped off under reduced pressure and the crude product was Soxhlet extracted in toluene to yield crystals, after

5   cooling, of (*t*-BuCp)2ZrCl2. Figs. 1 and 2 show the H' NMR traces (400 MHz) for Bis(i-propylcyclopentadienyl) Zirconium Dichloride and Bis(t-butylcyclopentadienyl) Zirconium Dichloride, respectively.

Example 2 - Preparation of Support Material

10   A solution of 10 wt% trimethylaluminum (TMA) in isopentane was sampled into a 3-l reaction flask equipped with a mechanical stirring device and an addition funnel containing a 200 g portion of a Davison D-948 silica. The silica had 9.7 wt% water content.

15   After complete addition of silica to the TMA solution at -5°C, the resulting suspension was stirred for a further 1 hour at 25°C before removing the isopentane solvent under reduced pressure to give a free-flowing stock support material comprising a methylalumoxane or

20   silica.

Example 3 - Supported Metallocene Catalysts

The procedure used for supporting (*n*-PrCp)2ZrCl2 and (*t*-BuCp)2ZrCl2 are similar; for example, 0.761 g (2.02 mmol) (*n*-PrCp)2ZrCl2 was dissolved in a

25   toluene/heptane (1:1, v/v) mixture. This solution was then added slowly over 40 minutes to a slurry of a 30 g portion of the support material prepared in Example 2 in 100 cm3 heptane. The reaction temperature was maintained at 60°C for an additional 1 hour before

30   drying the resulting catalyst to a free-flowing powder. The final catalyst has a loading of 0.6 wt% Zr and Al:Zr molar ratio of 76.

Examples 4-12: POLYMERIZATION TESTS

(a)   For each example a sample of metallocene supported by the method of Example 3 on the treated silica support material as described in Example 2 was used for ethylene homopolymerization and ethylene/1-butene

5   copolymerization.   In each case a continuous fluid bed gas-phase reactor operated at 300 psig (2.07 MPag) total pressure, 65°C reactor temperature and 0.7 ft/s (21.3 cm/s) cycle gas velocity was used for determining catalyst efficiency and response to co-monomer such as

10   1-butene.   A solution of TEAL (1 wt% in isopentane) was fed into the reactor as a scavenger at a rate of 1 cm3/h.   Details of ethylene and 1-butene composition, hydrogen concentration, catalyst addition rate and polymer production rate in the reactor for each Example

15   are included in Table I.   Polymer samples were collected and analyzed after three bed turnovers. (Example 11 and 12 are comparative in that no defined "first metallocene" is used which has a 2° or 3° carbon containing substituent.   The polymer produced is of

20   considerably narrower MWD than that produced in Examples 4-10.

TABLE I

Ex	Compound Used	C4 mol%	H2 ppm	Catalyst rate g/h	Polymer rate g/h	MI dg/min	d g/cc	Mw g/mol	MWD
4	(tBuCp)2ZrCl2	6.7	370	0.671	112	33.4	0.917	57700	8.3
5	(tBuCp)2ZrCl2	4.7	100	1.001	210	7.9	0.933	42700	5.9
6	(tBuCp)2ZrCl2	0	310	0.921	150	5.8	0.967	60600	4.9
7	(iPrCp)2ZrCl2	6.6	300	0.158	177	1.9	0.919	95500	5.6
8	(iPrCp)2ZrCl2	6.6	300	0.225	274	1.9	0.917	106500	4.5
9	(iPrCp)2ZrCl2	6.6	0	0.233	147	0.1	0.914	176300	8.8
10	(3PentCp)2-ZrCl2	4.5	200	0.156	161	4.3	0.921	75270	4.2
11	(iBuCp)2ZrCl2	6.1	300	0.501	297	2.5	0.907	85000	2.6
12	(nPrCp)2ZrCl2	6.4	380	0.361	280	1.4	0.909	102800	2.8

25   Molecular weight attributes (see Table I) were determined by using a Water's Associates Model 150C gel

40

permeation chromatographic (GPC) instrument. The measurements were obtained by dissolving polymer samples in hot trichlorobenzene (TCB) and filtering. The GPC runs were performed at 145°C in TCB at a flow
5 rate of 1 cm3/min. Styragel columns from Perkin Elmer, Inc. were used. The integration parameters were recorded using a Hewlett-Packard computer.

Example 13

Preparation of Support

10 Davison 948 silica (150 g, LOI 9.4%) was slowly added to a 10wt% solution of trimethyl aluminum (TMA) in isopentane (1077 cm3). The reaction temperature during silica addition was kept at -5oC. After complete addition of the silica, the temperature
15 was raised to 30oC and held for 1 hour. The solvent was then removed under reduced pressure until a free-flowing powder was obtained. This was saved and used as stock of support material comprising a methylalumoxane or silica.

20 ### Supporting (n-PrCp)2ZrCl2 on TMA-treated silica

A sample of the support material so described above (30 g) was suspended in 150 cm3 heptane in a reaction flask equipped with a dropping funnel containing 0.76 grams of (n-PrCp)2ZrCl2 in 20 cm3
25 toluene. The set-up was maintained at 60oC during the addition of the metallocene and held for 1 hour after complete addition of the metallocene. The solvents were then removed under reduced pressure to give a free-flowing powder. This catalyst had 0.6wt% Zr
30 loading.

Polymerization Test

The supported catalyst described above was used in gas-phase polymerization in the following manner and the results are summarized in Table 2.

Ethylene was co-polymerized with 1-butene in a fluid-bed reactor at 65ºC. During the polymerization, monomer feeds, hydrogen concentration and reactor pressure were kept constant. The gas velocity through

5 the reactor was 0.7 ft/s (21.3 cm/s). Catalyst was fed into the reactor at a rate that periodically brings the bed height in the reactor up to a set value for product discharge. Samples were taken and analyzed after at least three bed turnovers to determine the properties

10 of the polymer made.

Example 14

Supporting (t-BuCp)$_2$ZrCl$_2$ on TMA-treated silica

This catalyst was prepared in a manner similar to that described in Example 13. The following quantities

15 were used: 64.27 g of TMA-treated silica was suspended in 200 cm^3 heptane at 60ºC and 1.69 g of(t-BuCp)$_2$ZrCl$_2$ dissolved in 45 cm^3 toluene was slowly added to the slurry. Stirring was continued for 1 h after the metallocene solution had been added. The solvents were

20 removed under reduced pressure at 60ºC to give a free-flowing powder.

This supported (t-BuCp)$_2$ZrCl$_2$ catalyst was then tested

for ethylene/1-butene co-polymerization in a

25 manner similar to that used in Example 13.

Example 15

Preparation of supported (n-PrCp)(t-BuCp)ZrCl$_2$ catalyst

In a 500 cm^3 reaction flask equipped with a dropping funnel and a mechanical stirrer, n-BuLi (71

30 cm^3 of 1.6 M solution in hexanes) was slowly added to a solution of t-BuCp (13.61 g, 0.112 mol) in THF (130 cm^3). The resulting mixture was stirred at ambient temperature for 3 hours and then added slowly to ZrCl$_4$ (26.1 g, 0.112 mol) in 100 cm^3 THF at -78ºC. The

reaction mixture was allowed to slowly warm up to room
temperature over 15 hours.

A lithiated salt of nPrCp was prepared in a
separate 500 cm3 reaction flask by slowly adding 71 cm3
5 solution of 1.6M n-BuLi in hexanes to a solution of n-
PrCp (12.1 g, 0.112 mol) in 100 cm3 THF. After 3 hours
reaction time at ambient temperature, the lithiated n-
PrCp salt was slowly added to the reaction product of
the
10 t-BuCp⁻Li⁺ and ZrCl4 prepared as described above and
cooled to -78ºC. After complete addition of the
n-PrCp⁻Li⁺ salt, the reaction temperature was slowly
raised to 23ºC and stirring was continued for a further
15 hours. The volatiles were then removed under
15 reduced pressure and the crude product was extracted in
toluene/pentane to afford the pure compound.

A sample of the TMA-treated silica (45.9 g)
prepared as in example 13 above was suspended in 100
cm3 heptane at 60°C. (t-BuCp)(n-PrCp)ZrCl2 (1.216 g)
20 dissolved in 40 cm3 toluene was slowly added to the
suspension and stirring was continued for 1 hour after
the metallocene solution had been fully added. The
solvents were removed under reduced pressure to give a
free-flowing powder.

25 This catalyst was then used in ethylene/1-butene
polymerization as in Example 13 above.

Example 16

The supported catalyst described in Example 15 was
30 used in ethylene/1-butene co-polymerization in the
following manner. Ethylene was co-polymerized with 1-
butene in a semi-batch gas-phase reactor at 85ºC. The
pressure in the reactor was held constant by
continuously feeding 5 mole % mixture of 1-butene in

ethylene (Scott Specialty Gases) to compensate for any pressure change due to polymerization. After 1 hour, the polymer was separated from the seed bed material and analyzed for resin density and molecular weight

5 attributes.

Example 17

Mixed (n-PrCp)$_2$ZrCl$_2$ / (t-BuCp)$_2$Cl$_2$ Catalyst

A sample (12.6 g) of the supported (n-PrCp)$_2$ZrCl$_2$ catalyst described in Example 13 above was mixed with

10 12.6 g sample of the supported (t-BuCp)$_2$ZrCl$_2$ catalyst described in Example 2 above. This mixture was shaken well enough in flask to ensure a homogeneous mix of the two supported catalysts.

The resulting mixed catalyst was used for

15 ethylene/1-butene co-polymerization as described in Example 13 above.

Example 18

Mixed (n-PrCp)$_2$ZrCl$_2$ / (t-BuCp)$_2$Cl$_2$ Catalyst

A sample (30 g) of the support material described

20 in Example 13 was suspended in 100 cm^3 heptane at 60°C. A combination of (n-PrCp)$_2$ZrCl$_2$ (0.381 g) and (t-BuCp)$_2$ZrCl$_2$ (0.409 g) dissolved in 40 cm^3 toluene was slowly added to the slurry of the support. After complete addition of the metallocene solution, stirring

25 was a continued for an additional 1 h before the drying the catalyst to free-flowing powder under reduced pressure. The final catalyst had 0.6wt% transition metal loading with a ratio of the two metallocenes being 1:1.

30 The resulting catalyst was then used in ethylene/1-butene co-polymerization as described in Example 13 using a 300 ppm hydrogen concentration.

Example 19

Mixed (n-PrCp)$_2$ZrCl$_2$ / (t-BuCp)$_2$Cl$_2$ Catalyst

The catalyst described in Example 18 above was used for ethylene/1-butene co-polymerization as described in Example 13, but, using 50 ppm hydrogen concentration in the reactor.

TABLE 2

Example	Catalyst Rate (g/h)	Product Rate (g/h)	Efficiency[1] g/g	Density g/cc	M_W g/mol	MWD	Zr wt%	
							(t-BuCp)2 ZrCl2	(nPrCp)2 ZrCl2
13	0.364	355	975	0.909	102800	2.8	-	0.6
14	0.164	166	1013	0.910	89000	4.6	0.6	-
15	0.043	170	3910	0.904	98300	2.4	0.34*	0.26*
16	0.200	152	760	0.944	103800	2.6	0.34*	0.26*
17	0.097	254	2622	0.904	109000	3.0	0.3	0.3
18	0.189	177	936	0.906	80300	4.3	0.3	0.3
19	0.151	169	1118	0.905	130500	4.1	0.3	0.3

1. Efficiency at 150 psi; * The Zr loading takes into account the weight contribution of the t-Bu group relative to the n-Pr group.

Example 20

(n-PrCp)2ZrCl2 / (i-PrCp)2ZrCl2 Catalyst

A 20 gram sample of a 200°C silica gel was suspended in 120 cm3 toluene in a 500-cm3 reaction flask equipped with a stirrer and a dropping funnel. The flask was cooled to 0°C and 47 cm3 of a 30 wt% methyl-alumoxane (MAO) solution in toluene was added slowly. After 15 minutes, the temperature was raised to 70°C and the reaction continued for 3 h. Then 0.167 g (n-PrCp)2ZrCl2 combined in a vial with 0.667 g (i-PrCp)2ZrCl2 was dissolved in 25 cm3 toluene and the resulting homogeneous mixture of the metallocenes was added slowly to the suspension of the support at 70°C. Reaction continued for 1 hour and then solvent was removed under reduced pressure to give a free-flowing powder. This catalyst with 0.6 wt% Zr loading, 80% of which is due to the (i-PrCp)2ZrCl2 metallocene, was tested in a manner similar the one described in Example

16 for ethylene/1-butene polymerization; the results are shown in Table 3.

Example 21
$(n-PrCp)_2ZrCl_2$ / $(i-PrCp)_2ZrCl_2$ Catalyst

5 A 30 g sample of a 200°C silica gel was suspended in 200 cm³ toluene in a 500-cm³ reaction flask equipped with a stirrer and a dropping funnel. The flask was cooled to 0°C and 106 cm³ of a 30 wt% MAO solution in toluene was added slowly. After 15

10 minutes, the temperature was raised to 70°C and the reaction continued for 4 h. Then 0.377 g (n-PrCp)$_2$ZrCl$_2$ combined in a vial with 1.508 g (i-PrCp)$_2$ZrCl$_2$ was dissolved in 30 cm³ toluene and the resulting homogeneous mixture of the metallocenes was

15 added slowly to the suspension of the support at 70°C. Reaction continued for 1.5 h and then solvent was removed under reduced pressure to give a free-flowing powder. This catalyst with 0.75 wt% Zr loading, 80% of which is due to the (i-PrCp)$_2$ZrCl$_2$ metallocene, was

20 tested in a manner similar the one described in Example 16 for ethylene/1-butene polymerization; the results are shown in Table 3.

Example 22
$(n-PrCp)_2ZrCl_2$ / $(i-PrCp)_2ZrCl_2$ Catalyst

25 At 24°C, 1 kg of 200°C dehydrated silica was charged into an 8-liter reactor and 3.5 liters of a 30 wt% methyl-alumoxane in toluene was added followed by the addition of 3 liters of dried toluene. The temperature was then raised to 68°C and the mixture was

30 stirred for 4 hours. Then 49.5 g of (i-PrCp)$_2$ZrCl$_2$ mixed with 12.4 g (n-PrCp)$_2$ZrCl$_2$ and dissolved together in 300 cc of dry toluene was slowly added. Stirring continued for 2 more hours after all the metallocene solution had been added. The solvent was then removed

at the reaction temperature to afford a free-flowing
powder. A sample of the catalyst was tested for
ethylene/1-butene polymerization as described in
Example 16; the results are shown in Table 3.

5 **Example 23**

$(n-PrCp)_2ZrCl_2$ / $(i-PrCp)_2ZrCl_2$ Catalyst

A 20 g sample of a 200°C silica gel was
suspended in 120 cm^3 toluene in a 500-cm^3 reaction
flask equipped with a stirrer and a dropping funnel.

10 The flask was cooled to 0°C and 60 cm^3 of a 30 wt% MAO
solution in toluene was added slowly. After 15
minutes, the temperature was raised to 70°C and the
reaction continued for 4 h. Then 0.377 g (n-
PrCp)$_2$ZrCl$_2$ combined in a vial with 1.508 g (i-

15 PrCp)$_2$ZrCl$_2$ was dissolved in 25 cm^3 toluene and the
resulting homogeneous mixture of the metallocenes was
added slowly to the suspension of the support at 70°C.
Reaction continued for 1.5 h and then solvent was
removed under reduced pressure to give a free-flowing

20 powder. This catalyst with 0.75 wt% Zr loading, 70% of
which is due to the (i-PrCp)$_2$ZrCl$_2$ metallocene, was
tested in a manner similar the one described in Example
16 for ethylene/1-butene polymerization; the results
are shown in Table 3.

25 **Example 24**

$(n-PrCp)_2ZrCl_2$ / $(i-PrCp)_2ZrCl_2$ Catalyst

At 24°C, 800 g of 200°C dehydrated silica was
charged into an 8-liter reactor and 1570 cm^3 of a 30
wt% MAO in toluene was added followed by the addition

30 of 2 liters of dried toluene. The temperature was then
raised to 68°C and the mixture was stirred for 4 hours.
Then 22.1 g of (i-PrCp)$_2$ZrCl$_2$ mixed with 8 g (n-
PrCp)$_2$ZrCl$_2$ and dissolved together in 200 cc of dry
toluene was slowly added. Stirring continued for 1

more hours after all the metallocene solution had been added. The solvent was then removed at the reaction temperature to afford a free-flowing powder. A sample of the catalyst was tested for ethylene/1-butene

5 polymerization as described in Example 16 at different concentrations of aluminum alkyl on the seed bed; the results are shown in Table 3.

Example 25 & 26

(n-PrCp)2ZrCl2 / (i-PrCp)2ZrCl2 Catalyst

10 The catalyst described in Example 24 above was used for ethylene/1-butene co-polymerization as described in Example 16, but, at different levels of aluminum alkyl on the seed bed. The results are summarized in Table 23.

15 Example 27

(n-PrCp)2ZrCl2 / (i-PrCp)2ZrCl2 Catalyst

The catalyst described in Example 24 above was used for ethylene/1-butene co-polymerization as described in Example 13 with 700 ppm hydrogen in the

20 reactor. The results are summarized in Table 3.

Example 28

(n-PrCp)2ZrCl2 / (i-PrCp)2ZrCl2 Catalyst

A 16.5 g sample of a 200°C silica gel was suspended in 150 cm3 toluene in a 500-cm3 reaction

25 flask equipped with a stirrer and a dropping funnel. The flask was cooled to 0°C and 47 cm3 of a 30 wt% MAO solution in toluene was added slowly. After 30 minutes, the temperature was raised to 70°C and the reaction continued for 3 hours. Then 0.176 g (n-

30 PrCp)2ZrCl2 combined in a vial with 0.440 g (i-PrCp)2ZrCl2 was dissolved in 25 cm3 toluene and the resulting homogeneous mixture of the metallocenes was

added slowly to the suspension of the support at 70ºC.
Reaction continued for 1 h and then solvent was removed
under reduced pressure to give a free-flowing powder.
This catalyst with 0.5 wt% Zr loading, 70% of which is
5 due to the (i-PrCp)$_2$ZrCl$_2$ metallocene, was tested in a
manner similar the one described in Example 16 for
ethylene/1-butene polymerization; the results are shown
in Table 3.

Example 29 and 30

10 (n-PrCp)$_2$ZrCl$_2$ / (i-PrCp)$_2$ZrCl$_2$ Catalyst

A 20 g sample of a 200ºC silica gel was suspended
in 130 cm^3 toluene in a 500-cm^3 reaction flask equipped
with a stirrer and a dropping funnel. The flask was
cooled to 0ºC and 47 cm^3 of a 30 wt% MAO solution in
15 toluene was added slowly. After 30 minutes, the
temperature was raised to 70ºC and the reaction
continued for 3 hours. Then 0.493 g (i-PrCp)$_2$ZrCl$_2$
dissolved in 23 cm^3 toluene was added slowly to the
suspension of the support at 70°C.   Reaction continued
20 for 1 h and then 0.493 g (i-PrCp)$_2$ZrCl$_2$ dissolved in 23
cm^3 toluene was added slowly to the suspension of the
support at 70ºC. Reaction continued for 1 h and then
0.198 g (n-PrCp)$_2$ZrCl$_2$ dissolved in 23 cm^3 toluene was
added slowly. After 1 h, the solvent was removed under
25 reduced pressure to give a free-flowing powder. This
catalyst with 0.5 wt% Zr loading, 70% of which is due
to the (i-PrCp)$_2$ZrCl$_2$ metallocene, was tested in a
manner similar the one described in Example 16 for
ethylene/1-butene polymerization; Example 30 followed
30 this Example 29 except that 0.197 g(i-PrCp)$_2$ZrCl$_2$ and
.493 g (n-PrCp)$_2$ZrCl$_2$ were used; the results are shown
in Table 3.

Example 31

(n-PrCp)$_2$ZrCl$_2$ Catalyst

At 24°C, 680 g sample of 200°C dehydrated silica was charged into an 8-liter reactor and 1200 cm³ of a 30 wt% MAO in toluene was added followed by the addition of 2 liters of dried toluene. The temperature

5 was then raised to 68°C and the mixture was stirred for 4 hours. Then 16.5 g (n-PrCp)$_2$ZrCl$_2$ and dissolved in 200 cc of dry toluene was slowly added. Stirring continued for 2 more hours after all the metallocene solution had been added. The solvent was then removed

10 at the reaction temperature to afford a free-flowing powder. A sample of the catalyst was tested for ethylene/1-butene polymerization as described in Example 16. The results are shown in Table 3.

Example 32

15 **(i-PrCp)$_2$ZrCl$_2$ Catalyst**

A 20 g sample of a 200°C silica gel was suspended in 120 cm³ toluene in a 500-cm³ reaction flask equipped with a stirrer and a dropping funnel. The flask was cooled to 0°C and 90 cm³ of a 30 wt% MAO solution in

20 toluene was added slowly. After 45 minutes, the temperature was raised to 70°C and the reaction continued for 4 h. Then 1.32 g (i-PrCp)$_2$ZrCl$_2$ was dissolved in 30 cm³ toluene and added slowly to the suspension of the support at 70°C. Reaction continued

25 for 1 h and then the solvent was removed under reduced pressure to give a free-flowing powder. This catalyst was tested in a manner similar the one described in Example 16 for ethylene/1-butene polymerization; the results are shown in Table 3.

TABLE 3

Example	Alkyl on Bed[1]	Catalyst Rate	Product Rate[2]	Efficiency[2]	M_W	MWD	Zr wt%	
	(ppm)	(g/h)	(g/h)	(g/g)	(g/mol)		(iPrCp)2ZrCl2	(nPrCp)2ZrCl2
20	213	0.20	226	1131	80500	5.7	0.48	0.12
21	127	0.15	251	1670	84700	4.2	0.60	0.15
22	129	0.15	237	1582	86200	4.5	0.60	0.15
23	185	0.23	488	2123	74200	3.6	0.54	0.22
24	0	0.30	322	1076	77400	4.2	0.43	0.17
25	82	0.20	257	1283	87000	3.9	0.43	0.17
26	193	0.21	245	1169	82000	3.8	0.43	0.17
27	200	0.13	252	1924	33900	4.2	0.43	0.17
28	131	0.29	358	1234	66000	5.9	0.36	0.14
29	131	0.20	334	1672	72100	3.7	0.36	0.14
30	129	0.22	355	1614	76100	4.6	0.36	0.14
31	86	0.18	246	2887	67400	2.8	-	0.40
32	228	0.21	90	429	109500	10.5	0.70	-

1.   Aluminum alkyl concentration on polymer bed in the reactor (alkyl used as impurity scavenger)

2.   At 150 psi.

Example 33 - IMPROVED TENSILE IMPACT STRENGTH

For this Example, six polymers were produced by the catalyst and method of the present invention and two commercial type ethylene-butene copolymers were produced by prior art catalysts and methods, with the results presented in Tables IV, V and VI. The experimental copolymers, Polymers A-F, were produced in a gas phase reactor with a catalyst of the present invention, a bis(isopropyl cyclopentadienyl) zirconium dichloride or bis(t-butyl cyclopentadienyl) zirconium dichloride. The two commercial copolymers utilized as comparative controls, Polymers G-H, were produced in a fluidized bed gas phase reactor; example G with a Ti-based multisite catalyst, example H with a Cr-based multisite catalyst.

The structure of each copolymer is characterized by its density, molecular weight profile, and short-chain branching distribution. The processability of

each is indicated by its capillary rheology response;
its toughness, by its impact resistance.

All eight Polymers A-H fall within the 0.910-0.920
g/cc density range, as determined by ASTM D-792.

5   The principal structural distinction between
copolymers A-F and the commercial copolymers G-H is
intermolecular short-chain branching (SCB)
distribution. The Polymers A-F formed utilizing the
catalyst and method of the present invention all have

10   considerably narrower SCB distributions than the
controls, as evidenced by their high Composition
Distribution Breadth Indices (CDBI), low hexane
extractables (at equivalent density), and the absence
of any unbranched material (no homopolymer). Both

15   controls have very broad SCB distributions; each has a
low CDBI, high hexane extractables (at equivalent
density), and high homopolymer content. Narrow SCB
distributions are achieved with a metallocene-alumoxane
catalyst of the invention; broad SCB distributions are

20   common to all commercial, conventional Ziegler-type
catalyst used to produce linear polyolefins.

The most significant distinctions between Polymers
A-F of the present invention and the control Polymers G
and H are extractables, impact strength-processability

25   balance, and homopolymer content. At equivalent
densities, the lower extractables in the experimental
samples indicates that films made with these copolymers
will have lower reblock than films made with
conventional Ziegler-type catalyzed copolymers. At

30   equivalent Mw, the processability of the experimental
copolymers is slightly better than that of the Ti-based
commercial copolymer. At equivalent Mw, the tensile
impact of the experimental copolymers is approximately
three times higher than that of both conventional

Ziegler-type catalyzed copolymers. At equivalent
density, the very low homopolymer content in the
experimental copolymers indicates that films made with
these materials will have better clarity than films
made with conventional Ziegler-type catalyzed
copolymers.

The catalysts utilized in the present invention
are pure single site catalysts. FIG. 1 is a ^{1}H
NMR(400MHz) trace for (t-BuCp)ZrCl2 showing the methyl
protons of the t-butyl at about 1.25 ppm and showing
the protons on the Cp ring at about 6.3 ppm. FIG. 2 is
a 1H NMR(400MHz) trace for (i-PrCp)ZrCl2 showing the
methyl protons of the i-propyl at about 1.2 ppm, the
methine proton of the i-propyl at about 3.1 ppm, and
showing the protons on the Cp ring at about 6.2 ppm.

TABLE IV
Ethylene-Butene Copolymers Produced In A Single, Gas
Phase Reactor With Bis(R-Cp)2ZrCl2 Catalysts

Attribute	Polymer A	Polymer B	Polymer C
Cp R-group	i-propyl	i-propyl	t-butyl
density	0.916 g/cc	0.919 g/cc	0.919 g/cc
Mn	23,700	17,100	19,200
Mw	106,500	95,600	89,000
Mz	285,300	236,300	186,000
Mw/Mn	4.5	5.6	4.6
Mz/Mw	2.7	2.5	2.1
CDBI	56.8%	55.1%	54.5%
Hexane Extractables	4.1%	4.2%	13.3%
Homopolymer Content	<0.1%	<0.1%	<.01
Viscosity 190°C			
@13.7 s^{-1}	4550 Pa-sec	355 Pa-sec	3315 Pa sec
@34.2 s^{-1}	3175 Pa-sec	2655 Pa-sec	2380 Pa-sec
@68.3 s^{-1}	2290 Pa-sec	2045 Pa-sec	1810 Pa-sec
@137 s^{-1}	1640 Pa-sec	1475 Pa-sec	1325 Pa-sec
@342 s^{-1}	960 Pa-sec	905 Pa-sec	815 Pa-sec
Onset of Melt Fracture	342s^{-1}	683 s^{-1}	683 s^{-1}
Tensile Impact	347 ft-lb/in^2	282 ft-lb/in^2	345 ft-lb/in^2

TABLE V

Ethylene-Butene Copolymers Produced In A Single, Gas
Phase Reactor With Bis(R-Cp)$_2$ZrCl$_2$ Catalysts (con't)

5

Attribute	Polymer D	Polymer E	Polymer F
Cp R-group	t-butyl	i-propyl	i-propyl
density	0.910 g/cc	0.919 g/cc	0.914 g/cc
Mn	7,300	13,400	20,100
Mw	59,800	65,600	176,300
Mz	144,200	151,600	421,100
Mw/Mn	8.1	4.9	8.8
Mz/Mw	2.5	2.3	2.4
CDBI	60.9%	59.6%	61.8%
Hexane Extractables	N/A	N/A	N/A
Homopolymer Content	<0.1%	<0.1%	<0.1%
Viscosity 190°C			
@13.7 s^{-1}	1025 Pa-sec	1265 Pa-sec	14500 Pa-sec
@34.2 s^{-1}	835 Pa-sec	875 Pa-sec	8100 Pa-sec
@68.3 s^{-1}	710 Pa-sec	785 Pa-sec	(4380 Pa-sec)
@137 s^{-1}	580 Pa-sec	635 Pa-sec	(2260 Pa-sec)
@342 s^{-1}	390 Pa-sec	440 Pa-sec	(935 Pa-sec)
Onset of Melt Fracture	None Observed	3420 s^{-1}	34.2 s^{-1}
Tensile Impact	60 ft-lb/in^2	49 ft-lb/in^2	512 ft-lb/in

TABLE VI

Ethylene-Butene Copolymers Produced In A Single, Gas Phase Reactor With Commercial, Conventional Ziegler-Type Catalysts

Attribute	Polymer G	Polymer H
Cp R-group	Titanium-based	Chromium-based
density	0.918 g/cc	0.920 g/cc
Mn	31,800	14,000
Mw	105,600	99,500
Mz	279,800	398,400
Mw/Mn	3.3	7.1
Mz/Mw	2.7	5.5
CDBI	16.8%	25.9%
Hexane Extractables	9.9%	16.9%
Homopolymer Content	<15.0%	<23.7%
Viscosity 190°C		
@13.7 s^{-1}	4650 Pa-sec	3075 Pa-sec
@34.2 s^{-1}	3485 Pa-sec	1995 Pa-sec
@68.3 s^{-1}	2600 Pa-sec	1400 Pa-sec
@137 s^{-1}	1850 Pa-sec	980 Pa-sec
@342 s^{-1}	1105 Pa-sec	575 Pa-sec
Onset of Melt Fracture	683 s^{-1}	None Observed
Tensile Impact	110 ft-lb/in^2	85 ft-lb/in^2

The following figures illustrate data for the butene copolymers of the invention of Example 33.

FIG. 3 is a plot of log viscosity vs. log molecular weight for polymers of this invention (solid dot) and for conventional polymers produced by a heterogeneous catalyst of the conventional Ziegler-type catalyst. Viscosity is the key melt property that correlates with such processing parameters as extruder pressure, power draw, torque, etc. Viscosity was measured at 190°C and 340s^{-1}.

This plot shows that the processability of polymers of this invention and conventionally produced polymers are equivalent.

FIG. 4 is a plot of tensile impact vs. log molecular weight for polymers of this invention

(circles) and for conventional polymers produced by a
heterogeneous catalyst of the conventional Ziegler-type
catalyst (solid dots). The regression lines for the
polymers of this invention and for the conventional

5   Ziegler-type catalyst type polymers are represented by
dots and dashes, respectively. The ratio of the slopes
of the two linear regression curves is about 4
(1276.66/322.48= 3.959). Generally this ratio will be
at least about 1.5, preferably, at least about 2, and

10 most preferably at least about 4.

FIG. 5 is a plot of tensile impact ratio vs. log
molecular weight based on modeled data for the polymers
of this invention and for conventional Ziegler-type
catalyst type polymers. This shows that the polymers

15 of the present invention have at least twice the
tensile impact as the controls at a Mw of 60,000 (i.e.,
certain injection molding applications), and greater
that three times the tensile impact of the controls at
Mw greater than 70,000 (i.e. film applications). As

20 shown, the impact varies from about twice to about 3.6
times.

The polymers obtained in the process of this
present invention have significantly higher melt
strength than products produced with conventional

25 Ziegler-Natta catalysts or with metallocene catalysts,
which produce NMWD products as shown in the art in U.S.
Pat. No. 4,808,561 issued February 18, 1989 hereby
fully incorporated by reference. The following Table
VII describes seven NMWD copolymers produced with a

30 conventional Ziegler-Natta catalyst as is generally
known in the art or with a metallocene catalysts based
on bis(n-butyl cyclopentadienyl) zirconium dichloride
or bis(1-methyl-3-n-butyl cyclopentadienyl) zirconium
dichloride as is generally known in the art, along

with two LDPE's produced by the free-radical process as is known in the art, and a BMWD copolymer produced with the process of this present invention. The weight-average molecular weights (Mw) were measured with a

5 high temperature Gel Permeation Chromatograph. Melt tensile force was measured with a Rheotens Melt Tension Instrument.

Table VII
Melt Strength of Polyethylene

10

Polyethylene Type	Mw	Melt Tensile Force (cN)
NMWD/metallocene catalyst A	86260	2.8
NMWD/metallocene catalyst B	78700	2.0
NMWD/metallocene catalyst B	92300	2.5
NMWD/Ziegler-Natta catalyst	121210	5.2
NMWD/Ziegler-Natta catalyst	85900	2.0
NMWD/Ziegler-Natta catalyst	98920	3.0
NMWD/Ziegler-Natta catalyst	70620	1.0
LDPE/peroxide initiator	86300	8.4
LDPE/peroxide initiator	82200	6.5
BMWD/metallocene catalyst C	100440	9.4

The relationship between melt tensile force and molecular weight is illustrated in FIG. 9.

15 The melt tensile force of the NMWD copolymers is linearly proportional to Mw. The melt tensile force of the two LDPE's and the BMWD linear copolymer are all well above this linear model. The immediate consequence of high melt tensile force is high bubble stability

20 during blown film operations. Each of these three high melt strength products can be extruded into blown film at rates considerably faster than are achievable with the NMWD products.

Another distinctive attribute of products produced

25 in the present process is high film tensile force at low elongation. The following Table VIII describes a

linear low density and a linear medium density
copolymer produced with a conventional Ziegler-Natta
catalyst, and a low density BMWD copolymer produced in
the present process. Tensile properties were measured

5   with a United Film Tensile Tester; dart impact and
Elmendorf tear were measured according to ASTM D-1709
and D-1922, respectively.

Table VIII
LLDPE Blown Film Tensile Properties

10

Property	BMWD Product	Reference A	Reference B
MI	1.4	1.4	1.0
Density	0.918	0.918	0.935
MWD	Broad	Narrow	Narrow
Catalyst	Metallocene C	Ziegler-Natta	Ziegler-Natta
Tensile @ Yield (psi)*	1340	1400	2400
Tensile @ 20% Elongation (psi)*	1720	1640	
Tensile @ 100% Elongation (psi)*	2280	1470	
Dart Impact (g/mil)	165	160	55
Elmendorf Tear (g/mil)*	414	448	225

*Average: (MD+TD)/2

The traditional way to improve tensile stress at
15 low elongation is to increase crystallinity, i.e., to
increase density. However, when density is increased,
dart impact and Elmendorf tear both decrease. The
preceding table highlights the unusually high tensile
force at 100% elongation in the product produced with
20 metallocene C, a force which is close to the tensile
force at yield observed with the medium density
Ziegler-Natta copolymer. However, this BMWD product
does not show the same loss in dart and tear resistance
as the medium density Ziegler-Natta product.

The following FIG. 10 illustrates the stress-
strain profiles for the low density Ziegler-Natta
product and the low density BMWD product. The Ziegler-
Natta product shows the typical single yield point at
5   low elongation, followed by constant stress elongation,
strain-hardening, and then breakage. The BMWD product
shows a similar profile with one exception. Instead of
one yield point, it undergoes a double yield. The
tensile stress immediately after the second yield is
10   measurably higher than the stress in the Ziegler-Natta
product at the same elongation.

What is claimed is:

1.   A process for producing polyolefin which

comprises

            (a)   contacting olefin monomer, optionally
5   with co-monomer, with a catalyst system comprising:
                    (i)   a first transition metal
metallocene having a substituted cyclopentadienyl ring,
the substituent of which is a hydrocarbon group or
substituted hydrocarbon group comprising a 2° or 3°
10   carbon atom through which it is bonded to the ring; and
                    (ii) an activator for the metallocene
under polymerizing conditions to form the desired
polyolefin product.

2.   The process in accordance with claim 1
15   wherein component (i) of the catalyst system further
comprises a second transition metal metallocene having
a cyclopentadienyl ring that is substituted or
unsubstituted.

3.   The process in accordance with claim 2
20   wherein the second transition metal metallocene has a
cyclopentadienyl ring that is substituted with a
substituent which is a hydrocarbon group or a
substituted hydrocarbon group comprising a 2° or 3°
carbon atom through which the group is bonded to the
25   ring.

4.   The process in accordance with claim 1, 2 or
3 the first and/or second transition metal metallocene
is bridged.

60

5.   The process in accordance with any preceding claim wherein the ring substituent of the first or second metallocene is an alkyl group having from 3 to 20 carbon atoms.

6.   The process in accordance with claim 5 wherein the alkyl group has from 3 to 10 carbon atoms, preferably from 3 to 5 carbon atoms.

7.   The process in accordance with claim 6 wherein the alkyl group is t-butyl, i-propyl, or a 2° pentyl group.

8.   The process in accordance with any preceding claim wherein the metal of the first or second transition metal metallocene is independently selected from the group consisting of titanium, zirconium and hafnium.

9.   The process in accordance with any preceding claim wherein the activator (ii) comprises an alumoxane or an ionic activator.

10.   The process in accordance with any preceding claim wherein the first transition metal metallocene and/or the second transition metal metallocene is supported.

11.   The process in accordance with claim 10 when dependent on any one of claims 2 to 9 wherein the catalyst system comprises a supported first transition metal metallocene in physical admixture with a supported second transition metal metallocene.

61

12. The process in accordance with claim 10 when dependent on any one of claims 2 to 9 wherein the first and second transition metal metallocenes are carried on the same support.

13. The process in accordance with any preceding claim wherein the olefin monomer or the optional comonomer comprises ethene, propene, butene, pentene, hexene, heptene, octene or 4-methyl-1-pentene.

14. The process in accordance with any preceding claim when performed in solution, gas, or slurry phase.

15. The process in accordance with any preceding claim wherein the polyolefin product has a molecular weight distribution (MWD) greater than 4.

16. The process in accordance with claim 15 wherein the polyolefin product has an MWD of from 4-15.

17. The process in accordance with claim 16 wherein the polyolefin product has an MWD of from 5-10.

18.. The process in accordance with any preceding claim wherein the polyolefin product has a weight average molecular weight (Mw) greater than 50,000.

19. The process in accordance with claim 18 wherein the polyolefin product has an Mw of from 60,000-200,000, preferably from 80,000 to 180,000.

20. An impact resistant, optionally molded, article comprising a polyolefin product produced by the process in accordance with any preceding claim.

21. A film formed from a polyolefin product produced by the process in accordance with any of claims 1 to 19.

5

FIG. I

¹H NMR (400 MHz) of Bis(i-PropylCyclopentadienyl) Zirconium Dichloride

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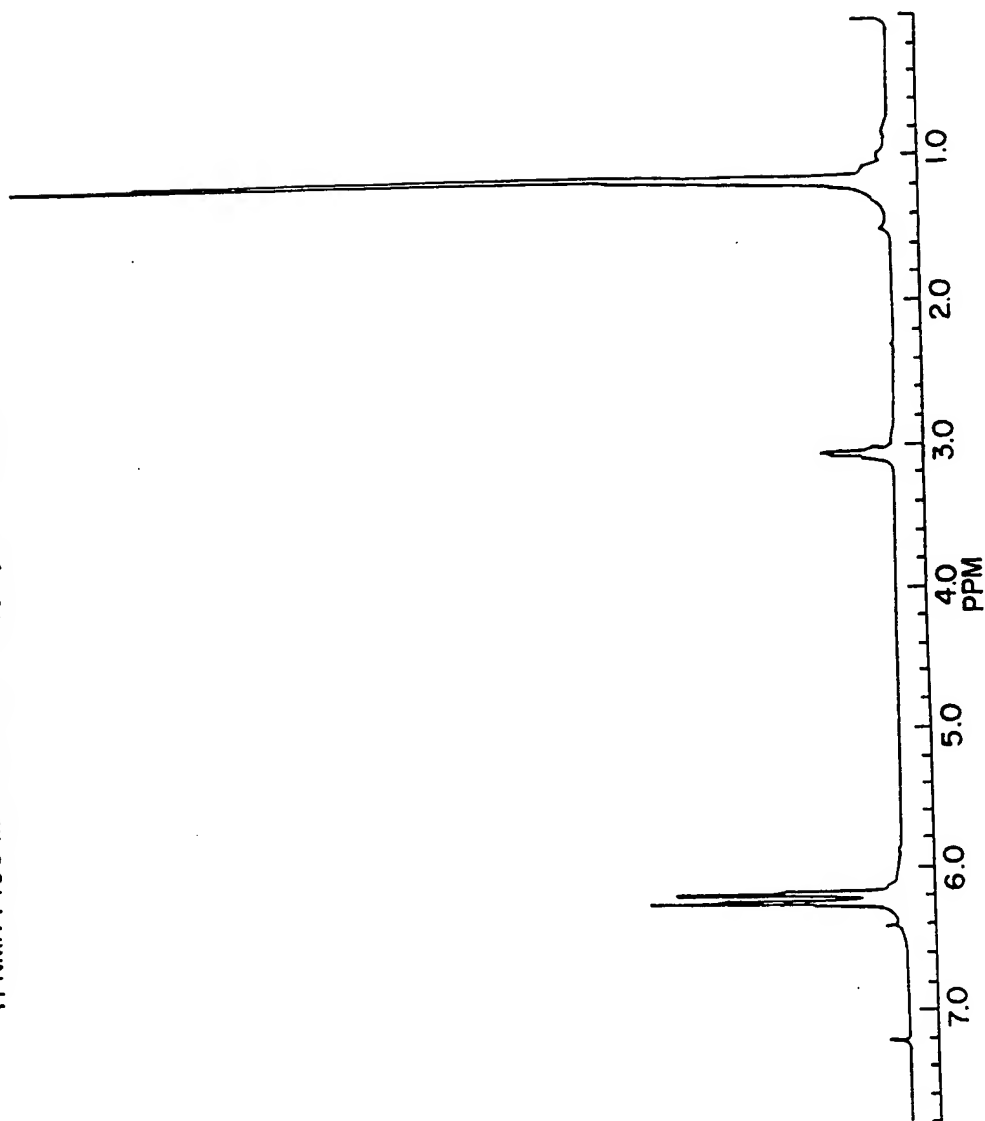
FIG. 2

^{1}H NMR (400 MHz) of Bis(t-Butyl(Cyclopentadienyl) Zirconium Dichloride

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FIG. 3
Linear Polyethylenes

● INVENTION
○ CONTROL
······ $-1.947166*X**2+20.706625*X-51.888391$

SUBSTITUTE SHEET
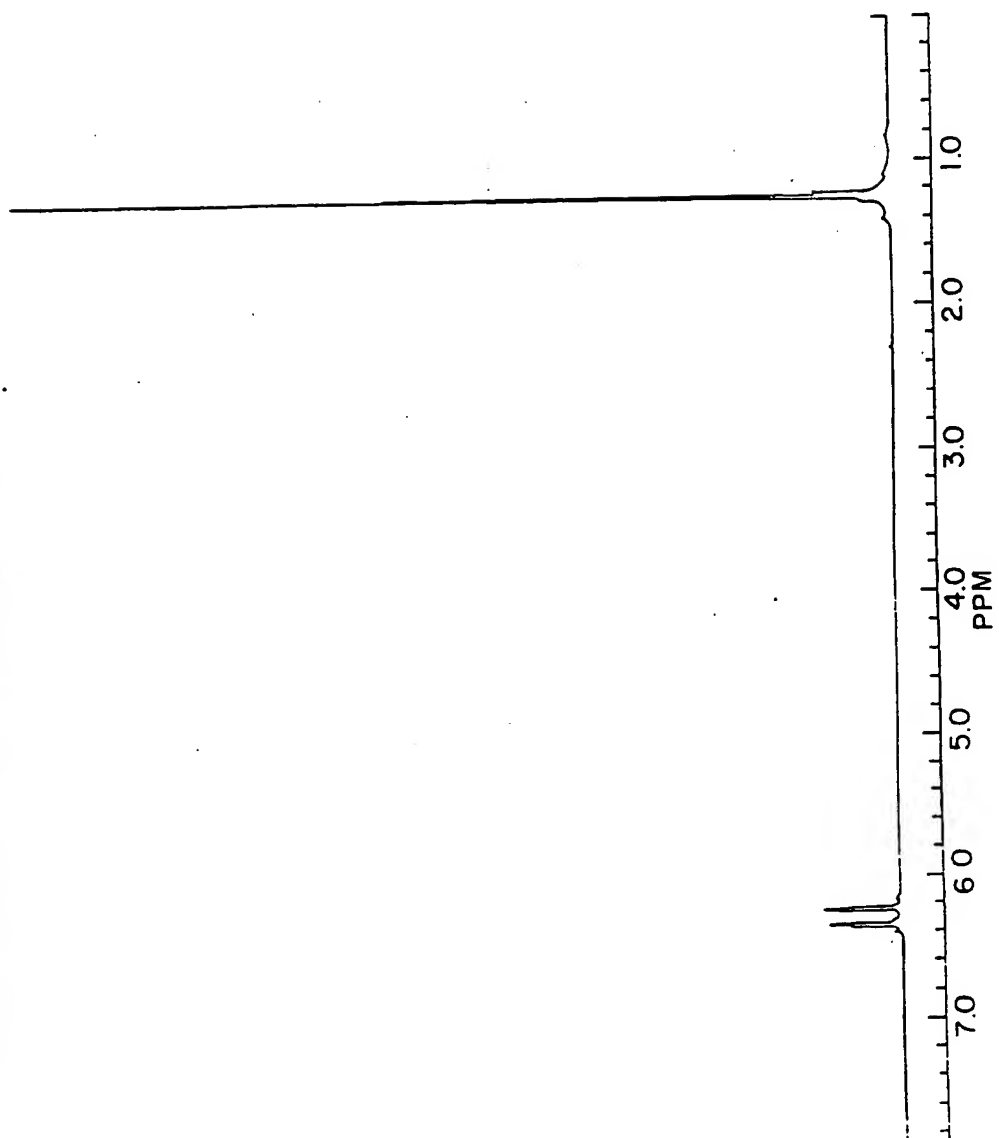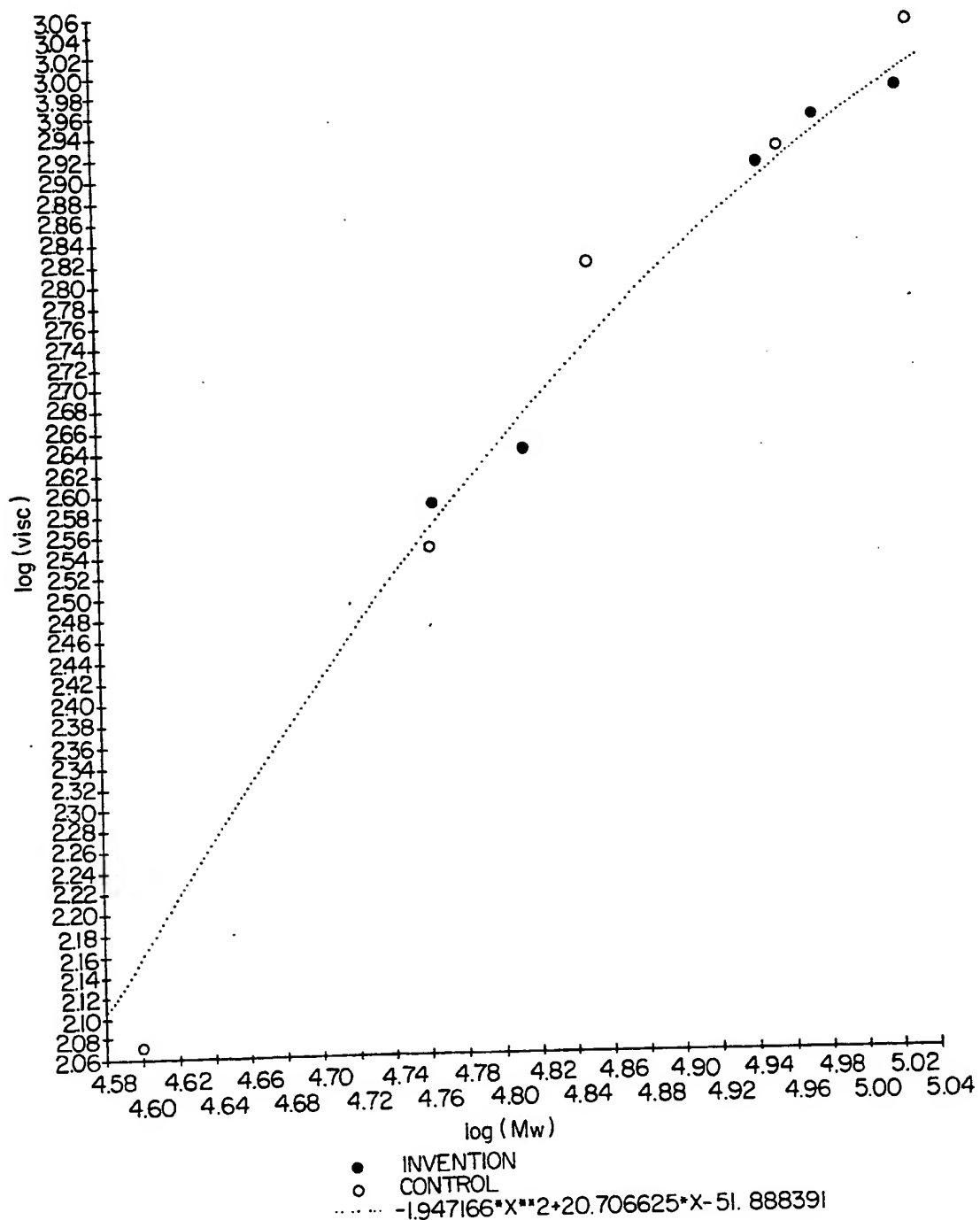
FIG.4
Toughness- Molecular Weight Balance

○　　INVENTION
●　　CONTROL
⋯⋯　1276.662237*X-6049.463214
-----　322.483457*X-1517.20058

4 / 9

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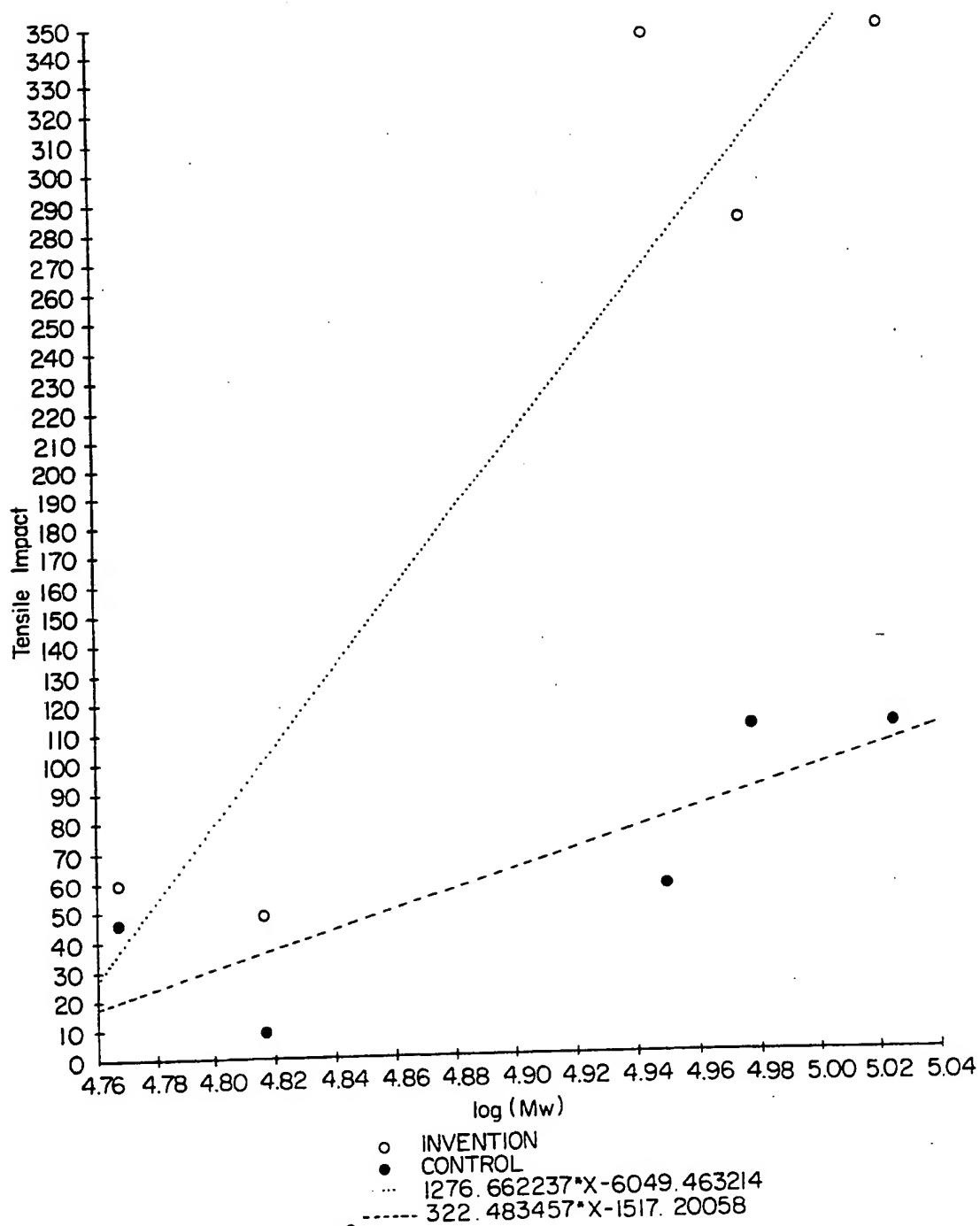
FIG. 5
Tensile Impact- Molecular Weight Advantage

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FIG.6

SDBI = 14.6°C
CDBI = 95.5%

X

SDBI = 29.4°C
CDBI = 42%

Y

IR RESPONSE, W

TIME MIN
0　　29　　58　　87　　116　　145

0　　0　4　　33　TEMP　62　TEMP °C　91　　120

>17.6　17.616　12　8　4　0 MOLE % COMONOMER

FIG. 8

CDBI = 72- 28 = 42%

71% →

50% →

29% →

Y

IR RESPONSE

TIME MIN.
0　　29　　58　　87　　116　　145

0　　0　4　　33　　62　TEMP °C　91　　120

17.6　17. 6 16　12　8　4　0 MOLE % COMONOMER

1.5CMED　CMED　0.5CMED

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FIG. 7

MOLE % COMONOMER=17.6 0.22094T
CORRELATION COEFFICIENT= 0.997
INTERCEPTS: 17.6%, 79.5°C

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FIG.9

Melt Tensile Force of Polyethylene vs. Molecular Weight

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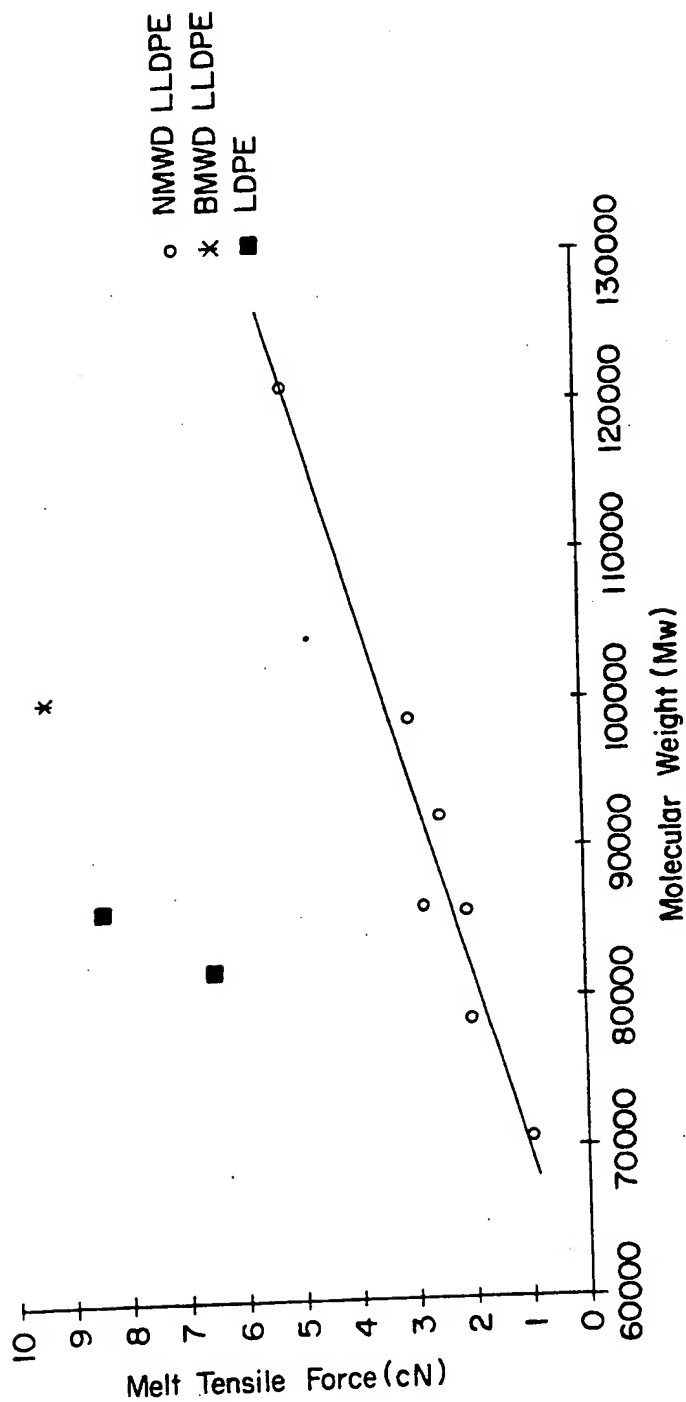
FIG. 10

Blown Film Stress-Strain Profiles

I. CLASSIFICATION OF SUBJECT MATTER   (if several classification symbols apply, indicate all)°

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.5   C 08 F 4/602   C 08 F 10/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl.5	C 08 F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category°	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP,A,0316155 (CHISSO CORP.) 17 May 1989, see claims; page 5, lines 53,54; page 6, lines 4,5,11,32,33,48,52; examples 6,7,8,9,10,11,22,23	1,3,5,6 ,7,8,9, 13,14
X	EP,A,0360492 (MITSUI PETROCHEM.) 28 March 1990, see claims; page 9, line 42	1,3,5,6 ,7,8,9, 13,14
A	EP,A,0310734 (FINA TECHN.) 12 April 1989, see claims; page 4, lines 15-19	1
A	EP,A,0436328 (MITSUI) 10 July 1991, see claims	

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
29-01-1993	2 2 FEB 1993
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer R. DE ROECK

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 9209250
SA 66664

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 11/02/93
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A- 0316155	17-05-89	JP-A- JP-A- JP-A- AU-B- US-A-	2076887 1319489 1301704 603268 4931417	16-03-90 25-12-89 05-12-89 08-11-90 05-06-90
EP-A- 0360492	28-03-90	JP-A- JP-A- JP-A- JP-A- US-A- CN-A-	2167305 2167306 2078687 2172991 4990640 1041597	27-06-90 27-06-90 19-03-90 04-07-90 05-02-91 25-04-90
EP-A- 0310734	12-04-89	JP-A- US-A-	1074202 4975403	20-03-89 04-12-90
EP-A- 0436328	10-07-91	None		

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